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ANNUAL REPORTS
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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Agr. Exper. Stat. Univ. Wisconsin</i>	Agricultural Experimental Station, University of Wisconsin.
<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Physik</i>	Annalen der Physik.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Phys.</i>	Annales de Chimie et de Physique.
<i>Ann. sci. Univ. Jassy</i>	Annales scientifiques de l'Université de Jassy.
<i>Anzeiger K. Acad. Wiss. Wien.</i>	Anzeiger der Kaiserliche Akademie der Wissenschaften in Wien.
<i>Apoth. Zeit.</i>	Apotheker Zeitung.
<i>Arch. Exp. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Hygiene</i>	Archiv für Hygiene.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles.
<i>Atti R. Accad. Sci. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Beitr. chem. Physiol. Path.</i>	Beiträge für chemische Physiologie und Pathologie.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft (Berlin).
<i>Bied. Centr.</i>	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Bio-Chem. J.</i>	The Biochemical Journal.
<i>Biochem. Zeit.</i>	Biochemische Zeitschrift.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i>	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Assoc. Chim. Sucr. Dist.</i>	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
<i>Bull. Coll. Agr. Tōkyō</i>	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
<i>Bull. Soc. Chim.</i>	Bulletin de la Société chimique de Paris.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Centr. Bakt. Par.</i>	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.

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ABBREVIATED TITLE.	JOURNAL.
<i>Centr. Min.</i>	Centralblatt für Mineralogie, Geologie und Palaeontologie.
<i>Chem. Centr.</i>	Chemisches Centralblatt.
<i>Chem. News</i>	Chemical News.
<i>Chem. Rev. Fett Harz Ind.</i>	Chemische Revue über die Fett- und Harz-Industrie.
<i>Chem. Weekblad.</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Föld. Közlöny</i>	Földtani Közlöny.
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Geol. Mag.</i>	Geological Magazine.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Jahrb. Min. Beil.-Bd.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
<i>Jahrb. Radioakt. Elek.</i>	Jahrbuch für Radioaktivität und Elektronik.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i>	Journal of Biological Chemistry.
<i>J. Chim. phys.</i>	Journal de Chimie physique.
<i>J. Fed. Inst. Brewing.</i>	Journal of the Federated Institutes of Brewing.
<i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Hygiene</i>	Journal of Hygiene.
<i>J. Landw.</i>	Journal für Landwirtschaft.
<i>J. Path. Bact.</i>	Journal of Pathology and Bacteriology.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Roy. Agric. Soc.</i>	Journal of the Royal Agricultural Society.
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Sanit. Inst.</i>	Journal of the Sanitary Institute.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>Landw. Versuchs-Stat.</i>	Die landwirtschaftlichen Versuchs-Stationen.
<i>Mem. R. Accad. Lincei</i>	Memoires della Reale Accademia dei Lincei.
<i>Milchw. Zentr.</i>	Milchwirtschaftliches Zentralblatt.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. Sci.</i>	Moniteur Scientifique.
<i>Pflüger's Archiv.</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Centr.-H.</i>	Pharmazeutische Centralhalle.
<i>Pharm. Weekblad</i>	Pharmaceutisch Weekblad.
<i>Pharm. Zeit.</i>	Pharmazeutische Zeitung (Berlin).
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Phys. Zeit.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Physiol. Soc.</i>	Proceedings of the American Physiological Society.
<i>Proc. Camb. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. Physiol. Soc.</i>	Proceedings of the Physiological Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Rec. trav. chim.</i>	Receuil des travaux chimiques des Pays-Bas et de la Belgique.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES. ix

ABBREVIATED TITLE.	JOURNAL.
<i>Rev. Metallurgie</i> . . .	Revue de Metallurgie.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . .	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Trans.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i> . . .	Transactions of the Faraday Society.
<i>Trans. Roy. Dubl. Soc.</i> . . .	Transactions of the Royal Dublin Society.
<i>Trans. Roy. Soc. Canada</i> . . .	Transactions of the Royal Society of Canada.
<i>Trans. Roy. Soc. Edin.</i> . . .	Transactions of the Royal Society of Edinburgh.
<i>Trans. Roy. Soc. S. Australia</i> . . .	Transactions of the Royal Society of S. Australia.
<i>Tsch. Min. Mitt.</i> . . .	Tschermak's Mineralogische Mittheilungen.
<i>U.S.A. Dept. Agric. Bull.</i> . . .	Bulletins of the Department of Agriculture, U.S.A.
<i>Wien. Sitzungsber.</i> . . .	Sitzungsberichte der Kaiserlich Akademie der Wissenschaften zu Wien.
<i>Woch. Brau.</i> . . .	Wochenschrift für Brauerei.
<i>Zeit. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeit. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeit. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeit. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeit. Farb. Text. Ind.</i> . . .	Zeitschrift für Farben- und Textil-Industrie.
<i>Zeit. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeit. Nahr. Genussm.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeit. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeit. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeit. Ver. deut. Zuckerind.</i> . . .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeit. Zuckerind. Böhm.</i> . . .	Zeitschrift für Zuckerindustrie in Böhmen.

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GENERAL AND PHYSICAL CHEMISTRY.

Laws of Chemical Stoichiometry.

THE Faraday Lecture, delivered by W. Ostwald,¹ has been subjected to a very adverse criticism by R. Nasini,² who not only rejects the main contention of Ostwald that the theoretical deduction of the laws of chemical stoichiometry is possible without the aid of the atomic hypothesis, but also makes objection to the validity of some of the definitions put forward by Ostwald. The conception of a chemical compound he considers to be quite independent of the range of its existence, and the deduction of the law of constant proportions from the conception of a chemical individual is regarded as illogical. Nasini also takes exception to the Ostwald definition of an element as a body which under all known conditions never gives any but hylotropic phases, as he considers that this definition would also include substances like silica and magnesium oxide.

Less adverse is the criticism offered by C. Benedicks,³ who recognises that the atomic hypothesis is not indispensable. He also seeks to give a deduction of the stoichiometric laws, the insufficiency of which is, however, pointed out by E. Baur.⁴ The latter, while regarding the Ostwald deduction as well-grounded, suggests an alternative method of deducing the stoichiometric laws based on the theory of simultaneous equilibrium.

Atomic Theory.

A very important paper, entitled "A Development of the Atomic Theory which correlates Chemical and Crystalline Structure, and leads

¹ *Ann. Report*, 1904, 1.

² *Gazzetta*, 1906, 36, i, 540.

³ *Zeit. anorg. Chem.*, 1906, 49, 284.

⁴ *Ibid.*, 50, 199.

to a Demonstration of the Nature of Valency," has recently been published by W. Barlow and W. J. Pope.¹ Satisfactorily to understand the theory now put forward, the original elaborate and closely reasoned paper must be read; but sufficient may perhaps be said here to give an indication of the basis of the theory, and the lines of its development.

The fundamental conception is that a chemical atom in a compound occupies a certain space or sphere of influence. Of these spheres of influence a crystallographically homogeneous structure can be built up, which can be subdivided homogeneously into units consisting of one or more of atomic spheres of influence. These units constitute the chemical molecule. From the form of aggregation of the spheres of atomic influence of the atoms associated in a molecule, the latter acquires a definite shape. From this standpoint, the authors investigate the formation of close-packed, homogeneous assemblages of spheres of atomic influence corresponding with different compounds; and since the close-packed assemblages must coincide in symmetry and relative dimensions with the crystalline structure of the particular substance, the method of partitioning the homogeneous assemblages into molecular units can be checked by crystallographic measurements.

A study of the methods by which one close-packed homogeneous assemblage of spheres may be converted, geometrically, by substitution of certain of its parts, into related close-packed homogeneous assemblages, shows that the atoms of the elements must be represented by spheres of influence directly proportional in volume to their fundamental valencies. These valency volumes, however, are not quite constant but undergo slight variation, for example, with the temperature. Further, differences are found in the volumes of the spheres of atomic influence in the case of elements having the same valency; and in passing from compound to compound the absolute magnitude of the spheres of atomic influence often change considerably, although the relative magnitudes are but slightly affected.

The properties of close-packed homogeneous assemblages of spheres lead, also, to an interpretation of multivalency and tautomerism, and throw light on the nature of ethylenic and acetylenic bonds and isomerism.

The authors have applied the geometrical principles which they have developed to benzene, triphenylmethane, naphthalene, anthracene, and their derivatives, and deduce a configuration for the benzene molecule which is in harmony with crystallographic and chemical evidence, and leads to an explanation of various features of the

¹ *Trans.*, 1906, **89**, 1675.

chemistry of the aromatic substances, including the meta-, ortho-, para-law of substitution.

Structure of Atoms.

Assuming the atom of an element to consist of a number of negative electrons in a sphere of uniform positive electrification,¹ J. J. Thomson² has investigated the theory of the dispersion of light, the scattering of Röntgen radiations, and the absorption of β -rays by gases. All three lines of investigation lead to the conclusion that the number of corpuscles in the atom is of the same order as the atomic weight of the element; whilst from the first method of investigation it is concluded that the mass of the carrier of unit positive charge is large compared with that of the carrier of unit negative charge. The data at present available indicate that the number of corpuscles in the atom is equal to the atomic weight; but as the evidence is rather indirect and the experimental data not very numerous, further investigation is necessary before one can be sure of the equality. The evidence seems, however, sufficient to establish the conclusion that the number of corpuscles is not greatly different from the atomic weight.

Change of Weight in Chemical Reactions.

During the past thirteen years not a few experiments have been carried out with great care by H. Landolt, A. Heydweiller, and others with the view of determining whether, in chemical reactions, the total weight of the reacting substances remains quite unchanged or undergoes appreciable alteration. As a general result, it was found that in the majority of cases there was a diminution of weight, which was frequently greatly in excess of the error of weighing. In order to determine whether this diminution of weight was due to experimental errors or stood in real connexion with the chemical change (owing, for example, to the escape of electrons or to a loss of material as in radioactive change), further experiments were undertaken by H. Landolt³ with such care that the greatest error attaching to an experiment is only ± 0.03 mg. As the total mass amounted to between 300 and 500 grams, the experimental error is only about one part in ten million.

Besides the U-shaped glass vessels formerly employed, similar vessels of quartz have been used in a few cases, and also vessels consisting of a beaker enclosed in a bulb surrounded by a vacuum mantle. Glass vessels coated internally with paraffin wax were also

¹ *Ann. Report*, 1904, 2.

² *Phil. Mag.*, 1906, [vi], 11, 769.

³ *Zeit. physikal. Chem.*, 1906, 55, 589.

employed in order to exclude any possible permeability of the vessel due to minute cracks or air-bubbles in the glass. The reactions studied and the results obtained are given in the following table :

Reaction.	Remarks.
$\text{Ag}_2\text{SO}_4 + 2\text{FeSO}_4 = 2\text{Ag} + \text{Fe}_2(\text{SO}_4)_3$ $3\text{AgNO}_3 + 3\text{FeSO}_4 = 3\text{Ag} + \text{Fe}_2(\text{SO}_4)_3 + \text{Fe}(\text{NO}_3)_3$	In most cases, a diminution of weight, exceeding the experimental error, the diminution being to a certain extent proportional to the mass of reacting substance. The diminution of weight was not observed, or was only slightly greater than the experimental error, when the vessel was coated internally with paraffin.
$\text{Fe} + \text{CuSO}_4 = \text{Cu} + \text{FeSO}_4$	In neutral and alkaline solution, no certain change.
$\text{AuCl}_3 + 3\text{FeCl}_2 = \text{Au} + 3\text{FeCl}_3$	No change.
$\text{HIO}_3 + 5\text{HI} = 6\text{I} + 3\text{H}_2\text{O}$	Always diminution of weight, in most cases, to an extent exceeding experimental error.
$2\text{I} + \text{NaHSO}_3 + \text{H}_2\text{O} = 2\text{HI} + \text{NaHSO}_4$	In most cases, no appreciable change.
$2\text{UO}_2(\text{NO}_3)_2 + 6\text{KOH} = \text{K}_2\text{U}_2\text{O}_7 + 4\text{KNO}_3 + 3\text{H}_2\text{O}$ Electrolysis of an aqueous solution of CdI_2 with alternating current of 3 amperes for 40 hours. Solution of ammonium chloride, potassium bromide, uranyl nitrate, chloral hydrate, in water. Precipitation of copper sulphate from its aqueous solution by alcohol.	No change.

Considering the results so far obtained by Landolt and by Heydweiller, it is found that diminution of weight occurs in 61 out of 75 cases, so that this behaviour appears to be the normal one ; any increase of weight which was found was always within the experimental error. The explanation of this behaviour Landolt seeks in the breaking up of the atoms on chemical change and in the escape of sub-atomic particles through the walls of the vessel. The diminution of weight does not appear to be due to the escape of electrons.

Chemical Affinity.

The chemical affinity is measured by the maximum external work done by a system (diminution of the free energy), not by the total heat of reaction, but J. N. Brönsted¹ develops a general equation for the affinity of a chemical reaction from which the value of the affinity at any temperature can be obtained from the curve of variation of the total heat effect with the temperature. In the case

¹ *Zeit. physikal. Chem.*, 1906, **55**, 371 ; **56**, 645.

where $dU/dT = c_1 - c_2$ (where U is the total heat effect, and c_1 , c_2 , the specific heat of the initial and final systems) the general expression

$$A = A_1 \frac{T}{T_1} - U_1 \frac{T - T_1}{T_1} + (c_2 - c_1) \left[T \log_e \frac{T}{T_1} - (T - T_1) \right]$$

is obtained, in which A_1 is the affinity at temperature T_1 . Making $T_1 = T_0$ (the transition temperature) one obtains the equation :

$$A = -U_0 \frac{T - T_0}{T_0} + (c_2 - c_1) \left[T \log_e \frac{T}{T_0} - (T - T_0) \right].$$

The formula is applied to the calculation of the free energy of transformation of the two forms of sulphur, the values so obtained being compared with those obtained from the relative solubilities of rhombic and monoclinic sulphur by applying the gas laws to the solutions, namely, $A' = 1.99 T \log_e (s/s')$ cal., where s and s' are the solubilities of monoclinic and rhombic sulphur respectively. The result is as follows :

t .	A (calculated).	A' (from solubilities).
0.0°	0.710	0.718
15.5	0.601	0.639
18.6	0.588	0.629
25.3	0.533	0.569

The formula has also been applied to the calculation of the affinity in the solution of lead chloride and potassium chloride in water, the affinities being deduced from measurements of electromotive force. Fair agreement was obtained in each case.

Equation of State.

The equation of van der Waals cannot, as is known, be taken as strictly true if the quantities a and b are regarded as specific constants, and L. Friderich,¹ therefore considers what modifications must be made if the van der Waals equation is still to be retained. From the assumption made by van der Waals that at the critical point the three roots of the equation become equal, one obtains $b = RT_c/8p_c$ and $\bar{b} = v_c/3$; but the values so obtained for b are generally widely divergent. Friderich therefore assumes that only two of the roots of the equation are equal, and deduces the equation :

$$b_c = -\frac{1}{2} \left(\frac{RT_c}{p_c} - 2v_c \right) + \sqrt{\frac{1}{4} \left(\frac{RT_c}{p_c} - 2v_c \right)^2 + \left(\frac{RT_c}{2p_c v_c} - 1 \right) v_c^2}.$$

By means of this equation the values of b_c have been calculated for a number of substances from the data of Young and his co-workers; and it is found that the ratio v_c/b is practically constant, with a mean

¹ *J. Chim. Phys.*, 1906, **4**, 123.

value of 2.442 for normal, non-associated liquids. Deviations from constancy are found in the case of associated liquids. Taking the ratio $v_c/b = 2.442$, the value of the ratio of the theoretical to the observed vapour density at the critical point is calculated to be 3.35 for non-associated liquids, and with the help of this value the factor of association in the case of associated liquids can be calculated.

The equations of Friderich allow of the calculation of the values of a and b only at the critical point, but with the help of the data for isopentane Friderich has calculated the value of a at temperatures other than the critical. The values so obtained, however, show that a cannot be regarded as a function only of the volume, but that it must also depend on the temperature and pressure as well.

Modifications of the van der Waals formula have also been suggested by A. Batschinski.¹

Vapour Pressure and Chemical Composition.

For the calculation of the vapour pressure curve of a substance, E. C. Bingham² finds that very satisfactory values are given by the equation, suggested by Nernst,

$$\log \pi/p = 1.75 \log \tau/T + a' \left[(\tau/T - 1) - \frac{1}{2.36} \left(1 - \frac{T}{\tau} \right) \right],$$

in which a' is a constant the value of which varies from substance to substance. This expression enables one to calculate the vapour pressure curve from a knowledge of the critical temperature and pressure and the value of the vapour pressure at any given temperature, such as the boiling point. From an examination of a large number of substances, it is found that the values of Ma' (where M is the molar weight) can be calculated additively, with fair approximation, from "atomic" values of a' , so that $Ma' = 42l + 1.9m + 41n \dots$, where l , m , $n \dots$ are the number of atoms of carbon, hydrogen, oxygen, &c., respectively, in the molecule.

The same subject is treated by H. von Jüptner,³ who shows that the value of a in the equation of van der Waals (see p. 21) first decreases to a minimum with rising temperature, and thereafter increases. The initial diminution of a can be represented by a straight line, and the succeeding increase by a circle the radius and position of which vary for different substances. Two equations are therefore developed, one holding for temperatures up to that at which a is a minimum, and the other for temperatures above this.⁴

¹ *Ann. Phys.*, 1906, [iv], **19**, 307, 310; **21**, 1001.

² *J. Amer. Chem. Soc.*, 1906, **28**, 717.

³ *Zeit. physikal. Chem.*, 1906, **55**, 738.

⁴ Compare also P. A. Guye, *ibid.*, 1906, **56**, 461.

Heat of Vaporisation and Boiling Point.

It has been shown by Nernst (see p. 21) that the value of the molecular heat of vaporisation divided by the absolute temperature of the boiling point varies with the latter, and E. C. Bingham¹ finds, from an investigation of a large number of substances, that, with the exception of hydrogen and a few other substances for which the values are uncertain, the values of Trouton's constant, $\frac{\lambda}{T}$, increase as a linear function of the temperature of the boiling point according to the equation $\lambda/T = 17 + 0.011T$. In the case of associated liquids, the values of λ/T are considerably greater than those given by this formula, and the divergences are considered by Bingham as a measure of the association. In the case of the alcohols, the divergences are practically the same, whilst in the case of water, the acids, and nitric oxide, they are much greater.

A new determination of the heat of vaporisation of water between the temperatures 30° and 100° has been made by F. Henning.² He considers that his results, which can be represented by the formula $L = 94.210 (365 - t)^{0.37249}$ cal., are correct to 1 per mille.

Osmotic Pressure.

During the past year the subject of osmotic pressure of solutions has received not a little attention, both on the experimental and the theoretical side. In a paper "On the Nature of the Process of Osmosis," L. Kahlenberg³ communicates a large number of qualitative experiments to demonstrate that the action of the semi-permeable membrane in osmotic experiments depends on its selective solubility for solute and solvent. Quantitative measurements were also made, using caoutchouc membranes and solutions of sucrose, lithium chloride, and silver nitrate in pyridine, and it was found that concordant results could only be obtained when the solutions were stirred, a behaviour which the author attributes to the want of uniformity in the concentration of the solution in the cell; the solution on the inner surface of the membrane being more dilute than in the body of the solution owing to the diffusion inwards of the solvent from outside. As the result of his measurements, Kahlenberg concludes that the gas laws do not hold at all for solutions, neither with regard to concentration nor to temperature; and the theory of electrolytic dissociation is also rejected by the author, because he found that solutions of lithium chloride gave lower pressures than solutions of sucrose.

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 723.

² *Ann. Physik.*, 1906, [iv], **21**, 849.

³ *J. Physical Chem.*, 1906, **10**, 141.

This paper by Kahlenberg was made the subject of discussion by W. C. D. Whetham and by the Earl of Berkeley and E. G. J. Hartley. The first-mentioned¹ recalled the principles on which the theory of osmotic pressure rests. From the experimental relation between the solubility of a gas and the pressure, van't Hoff showed that, on the basis of the second law of thermodynamics, the osmotic pressure of a dilute solution must possess the same value as the ordinary pressure of a gas at the same concentration, provided the solution is so dilute that the dissolved systems, each made up of a particle of solute as nucleus, and the portion of the solvent which it influences, are beyond each other's sphere of action. No assumption is made as to the nature of osmotic pressure, although Kahlenberg seems to consider that the thermodynamic theory of solutions stands or falls with the hypothesis that the pressure is due to molecular bombardment. The position taken by Kahlenberg, that because a perfect semi-permeable membrane does not exist, a theory which postulates one cannot be maintained, Whetham refuses to adopt. Further, to the statement made by Kahlenberg that the opponents of the van't Hoff idea have generally held that the so-called osmotic pressure is an ordinary hydrostatic pressure brought about by the entrance of liquid into the osmotic cell, Whetham replies that this is the view which is also held by van't Hoff and his supporters.

With regard to the brushing aside by Kahlenberg of the theory of ionic dissociation, Whetham remarks that the free existence of the ions (though possibly or probably combined with the solvent) is required by the electrical phenomena; that the theory rests on electrical evidence, and must be tried by such.

In their discussion of Kahlenberg's paper, Lord Berkeley and E. G. J. Hartley² point out that the statement made by Kahlenberg that the indirect measurement of the osmotic pressure from vapour tensions involves the assumption that the gas laws holds for solutions is contrary to fact. They have shown (*infra*) that aqueous solutions of sucrose give the same value of osmotic pressure whether observed directly or deduced indirectly from the vapour pressures; and the relation connecting osmotic pressure and vapour pressure is quite independent of the gas laws holding for solutions. The authors also call attention to a typical experiment from which Kahlenberg draws his conclusion against the theory of van't Hoff, namely, an experiment dealing with the osmotic pressure of sucrose in pyridine. From Kahlenberg's statement that sugar was found outside the membrane, the authors calculate that the amount found would correspond with a fall in the pressure gauge of 20 cm. per second, which would account for the fact that the theoretical pressure was not reached.

¹ *Nature*, 1906, **74** 54.

² *Ibid.*, 54.

Kahlenberg¹ will not accept the calculation of Lord Berkeley and Hartley, and does not consider that the application of thermodynamic reasoning to actual osmotic processes can be applied, because it involves the assumption of a membrane which is semi-permeable, and at the same time passive, whereas his experiments show it to have selective action.

[To the writer of this Report, it appears that the objection of Kahlenberg depends on a misunderstanding of the meaning of a thermodynamically passive membrane.]

In their previous very careful work on the osmotic pressure of solutions of sucrose, H. N. Morse and J. C. W. Frazer² pointed out certain sources of error which were present, namely, thermometer effects, or temporary fluctuations of pressure which follow changes of temperature; uncertainty as to the volume at the head of the manometer; sugar inversion. The above-mentioned authors, in co-operation with B. S. Hopkins,³ have now described in great detail the precautions which they have taken to avoid the above errors. In carrying out their latest measurements an additional source of error was met with, namely, the growth of *Penicillium glaucum*. It was found, however, that the growth of this fungus could be entirely prevented by the addition of thymol in quantities so small as not appreciably to affect the osmotic pressure. With regard to the driving of the air from the pores of the cell by electric endosmose, better results are now found to be obtained with solutions of lithium chloride than with the potassium sulphate formerly employed.

In extension of previous measurements⁴ H. N. Morse, J. C. W. Frazer, E. J. Hoffman, and W. L. Kennon⁵ have carried out an exceedingly careful redetermination of the osmotic pressure of solutions of sucrose of various concentrations, using a thermostat (described in the preceding paper) and with the elimination as far as practicable of all known errors. The amount of inversion taking place in the sugar solutions was determined polarimetrically, and the necessary correction introduced. The results, which the authors consider to be as precise as they can hope to obtain under the present conditions, confirm their previous conclusion that sucrose, in aqueous solution, exerts an osmotic pressure equal to that which it would exert if it were gasefied at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state. It is, however, uncertain whether the standard for the volume of the solvent is its volume at maximum density or at the prevailing temperature.

The following table gives the results obtained. In connexion with

¹ *Nature*, 1906, **74**, 222.

² *Ann. Report*, 1905, 7.

³ *Amer. Chem. J.*, 1906, **36**, 1.

⁴ *Ann. Report*, 1905, 6.

⁵ *Amer. Chem. J.*, 1906, **36**, 39.

this it should be again noted that the gram-molecular volume of hydrogen is taken as 22.488 litres, and the molecular weight of sucrose is taken as 339.60 (on the basis of $H = 1$).

Weight-normal concentration. (moles in 1000 grams of solvent).	Observed osmotic pressure (atm.).	Theoretical gas pressure at same temperature (atm.).	Mean molar weight, calculated from osmotic pressure.
0.1	{ 2.51 2.55 4.72 }	{ 2.42 2.43 4.79 }	325.21
0.2	{ 4.78 4.81 7.24 }	{ 4.80 4.81 7.21 }	341.87
0.3	{ 7.20 9.64 9.69 }	{ 7.16 9.61 9.63 }	338.29
0.4	{ 12.06 12.22 14.74 }	{ 12.06 12.10 14.55 }	337.89
0.5	{ 14.70 14.77 16.95 }	{ 14.55 14.54 16.94 }	335.24
0.6	{ 16.96 19.30 19.39 }	{ 16.93 19.35 19.36 }	339.55
0.7	{ 21.82 21.91 24.42 }	{ 21.86 21.86 24.19 }	339.78
0.8	{ 24.05 24.05 24.05 }	{ 24.28 24.28 24.28 }	339.51
0.9			339.56
1.0			
Mean			337.59

In connexion with the value given above for the molar weight in 0.1 normal solution, it should be remarked that in 1905 the mean value obtained was 336.8.

With regard to the freezing point of solutions of sucrose, previous results are confirmed that the depression of the freezing point is not only proportional to the weight-normality of the solution but also to the density. In the case of solutions of dextrose the depression is stated to be proportional to the weight-normality only. Further experiments are promised.

In addition to the above, direct measurements of the osmotic pressure of solutions of sucrose have also been carried out by the Earl of Berkeley and E. G. J. Hartley.¹ The method which they employ is, in general principle, to determine the mechanical pressure which must be applied to the solution to prevent inflow of solvent. Solutions of sucrose, dextrose, galactose, and mannitol were studied, in concentrations varying from 100—750 grams per litre of solution, corresponding with osmotic pressures of 13—130 atmospheres. In their experiments account was taken of leakage and also of the passage of sugar through the membrane. In confirmation of the

¹ *Phil. Trans.*, 1906, 206, A, 481.

validity of the method, the equilibrium pressure was determined between two solutions of sucrose containing 750 and 540 grams per litre respectively. The equilibrium pressure observed was 66.0 atm., whilst the difference between the osmotic pressures observed against pure water was 66.23 atm.

It was found that in all cases the observed osmotic pressures were greater than those calculated from the "gas law" formula, but approach tangentially to these values in dilute solutions. The values obtained are somewhat higher than those recorded by Morse and his co-workers (*supra*).

Lord Berkeley and E. G. J. Hartley¹ have also carried out an indirect determination of the osmotic pressure of solutions of sucrose from measurements of the vapour pressure. For the calculation of the osmotic pressure, the authors deduce the equation $P = \frac{As}{\sigma} \cdot \log p/p'$,

where A is the pressure of the standard atmosphere, s the density of water at the temperature of the experiment, σ the density of water-vapour, and p and p' the vapour pressure of the water and of the solution respectively. This differs from the equation proposed for dilute solutions by Arrhenius in that the specific volume of the solvent is substituted for the specific volume of the solution. The results obtained agree with those determined directly to within 5 per cent.

* A thermodynamic deduction of the relation between the osmotic pressure (under the pressure of the vapour) and vapour pressure has been given by W. Spens,² who deduces the equation $Pv_s = sp \log p/p'$, where P is the osmotic pressure, v_s the increment in volume of a large mass of solution when unit mass of the solvent is added. The expression becomes identical with that of Lord Berkeley and Hartley only when the contraction on dilution is negligible.

Reference should also be made to a paper by J. J. van Laar,³ who shows how the results obtained by Morse and his co-workers agree with his theoretical deductions.

Theory of Solutions.

In connexion with the large amount of discussion, just referred to, which has taken place regarding osmotic pressure and the van't Hoff theory, good service has been done by W. D. Bancroft,⁴ in recalling what were the assumptions made by van't Hoff. In the formula deduced by van't Hoff, $PV = RT \frac{N}{n} \log p/p'$, the assumptions made were

¹ *Proc. Roy. Soc.*, 1906, **77**, A, 156.

² *Ibid.*, 234.

³ *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **14**, 849.

⁴ *J. Physical Chem.*, 1906, **10**, 319.

that the vapour of the solvent follows the gas laws, and that the volume of the liquid can be neglected in comparison with that of the vapour when calculating the work done in an isothermal distillation. V , in the above equation, is the volume through which the piston moves in squeezing out the amount of solvent in which one molecular weight of the solute is dissolved, and becomes equal to the volume of the solution only when the latter is infinitely dilute. This explains why Morse and his co-workers obtained better values for the calculated molecular weight when they used the volume of the solvent instead of that of the solution in their calculations (*supra*). Morse and his co-workers, however, have overlooked the fact that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the components of the solution are mixed.

Further, by postulating $PV = RT$, one obtains the van't Hoff-Raoult equation $\frac{n}{N} = \log p/p'$, where n is the grams of solute divided by its molar weight in solution, N the grams of solvent per molar weight of solute divided by the molar weight of the solvent in the state of vapour. This holds, however, only when the heat of dilution is negligible. The thermodynamic equation shows¹ that in determinations of the molar weight by the freezing point method, where there is marked evolution of heat on dilution, we shall expect to find an abnormally high osmotic pressure, and to calculate an abnormally low molar weight. The molar weights determined at infinite dilution are correct, but all others are in error to a greater or less extent. On allowing for the heat of dilution, the author finds that the abnormal molar weights for sodium in mercury (Ramsay), for sulphuric acid in water, for resorcinol in alcohol, for cupric chloride in water, and for alcohol in benzene are due wholly or in part to the heats of dilution.

On the basis of the regularities obtained by Caldwell (p. 28) in the inversion of sucrose by acids, H. E. Armstrong² also seeks to justify the use of the volume of solvent, in place of the volume of solution, in the calculation of osmotic pressures, and in the study of the quantitative influence of substances in solution.³ The author considers that in ordinary water there is an equilibrium represented by $(\text{H}_2\text{O})_n \leftarrow n\text{H}_2\text{O}$, in which n may have several values.⁴ Introduction of any soluble substance involves the disturbance of this equilibrium in the direction $(\text{H}_2\text{O})_n \rightarrow n\text{H}_2\text{O}$, and the "osmotic pressure" is the measure of the extent to which equilibrium is thus disturbed.

¹ Compare J. E. Trevor, *infra*.

² *Proc. Roy. Soc.*, 1906, **78**, A, 264.

³ Compare Cohen, *Zeit. physikal. Chem.*, 1897, **23**, 442.

⁴ Compare W. Sutherland, p. 13.

The monads are to be regarded as the attracting element in the region of the solution, and as conditioning a flow of similar molecules from the region of the pure solvent, or more dilute solution, until the two regions are in equilibrium. Over and above this, there is, in the case of electrolytes, the attraction of the dissolved substance for the solvent. On this hypothesis, electrolytes are substances which are attractive of water practically in proportion to the efficiency of their solutions as electrolytes.

Mention may also be made of a paper by G. Zemplén,¹ who concludes from measurements of the surface tension of aqueous solutions of silver nitrate, carbamide, and sodium chloride that water has the same degree of association in its solutions as when pure.

A mathematical treatment of the general equations of the theory of solutions has been given by J. E. Trevor.²

Aqueous Solutions of Electrolytes.

In a theory of the "Molecular Constitution of Aqueous Solutions" put forward by W. Sutherland,³ the contraction occurring when an electrolyte is dissolved in water is attributed to its changing some of the trihydrol into dihydrol. Positive ions change trihydrol into dihydrol, while negative ions change dihydrol into trihydrol. If λ represents the ionic velocity, K the dielectric capacity of the stuff of the ion, B the limiting volume of the gram atom, and τ the number of gram-molecules of trihydrol changed to dihydrol by a gram-equivalent of solute, the expression $\tau/(\lambda KB^{\frac{2}{3}})^{\frac{1}{2}}$ is constant for positive ions, and $\tau/(\lambda KB^{\frac{2}{3}})^{\frac{1}{2}}$ is constant for negative ions. The author also considers that the large apparent velocity assigned to hydrion and hydroxidion are not the true velocities.⁴ Both ions cause water to dissociate, and at the ordinary temperature the ionic velocity hitherto assigned to hydrion is 2.92 times its true value, and that assigned to hydroxidion is 1.92 times its true value. The true velocities conform to the law $\lambda B^{\frac{2}{3}}K/\nu$ where ν is the valency.

The departure of specific heats of solutions from the mixture law is also traced to the change of trihydrol into dihydrol.

On the assumption that the ions in a solution are hydrated, W. R. Bousfield⁵ has deduced the following relation between the average radius of the hydrated ion and the dilution $r=r_{\infty}(1+Bh^{-\frac{2}{3}})^{-1}$, where h is the hydration. To this function, r , the author gives the name radion, and shows that the densities of solutions of potassium chloride and sodium chloride can be expressed by the same formula as

¹ *Ann. physik.*, 1906, [iv], 20, 783.

² *J. Physical Chem.*, 1906, 10, 392.

³ *Phil. Mag.*, 1906, [vi], 12, 1.

⁴ Compare Daneel, *Ann. Revoort*, 1905, 24.

⁵ *Phil. Trans.*, 1906, 206, A, 101.

a function of the radions. Further, the reciprocals of the Hittorf migration numbers are expressible as a linear function of the radions, and a relation has also been established between the viscosity of dilute solutions of potassium and sodium chloride and the radions.

Defining the effective molecular freezing point depression as the ordinary so-called molecular depression divided by $(1 + a)$, where a is the ionisation, and denoting this by D , one obtains $D = 1.86 + C(I_{\infty} - I_v)$, where I_v and I_{∞} are the ionic volumes (proportional to the cubes of the radions) at dilution v and at infinite dilution, and C is a constant. Between solution volume and effective freezing point depression there exists the relation $D = 1.86 + 3.38V_s$ where δV_s is the change in solution volume for different dilutions. Lastly, as an expression holding both for potassium and sodium chlorides, the formula is deduced $\frac{h}{a} / \left(\frac{h}{1-a} \right)^{\frac{2}{3}} = 3.197$.

Reference may also be made here to a theory of electrolytic dissociation worked out by M. Brillouin¹ on the assumption that the ions or molecules occupy cavities within the solvent.

Conductivity of Aqueous Solutions of Electrolytes.

By expressing the concentration in gram-equivalents per gram or kilogram, instead of per cubic centimetre or litre of solution, J. Gibson² obtains for the equivalent conductivity of solutions of good electrolytes the expression $\Lambda_M = a + b\Gamma$, where Λ_M is the equivalent conductivity expressed, as stated, in mass units, Γ the concentration in gram-equivalents per kilogram of solution, and a and b are constants for each electrolyte. This relation has been tested by means of available data in the case of a large number of strong electrolytes, acids, bases, and salts, in concentrations ranging from about 0.5 to about 7 gram-equivalents per kilogram of solution. Of the forty-nine electrolytes examined, zinc chloride and cadmium chloride are marked exceptions, whilst cadmium bromide is less exceptional. Of the remaining forty-six electrolytes, the differences between the calculated and observed values of the conductivity are in most cases under 1 per cent., and in no case greater than 2.1 per cent. Further, by means of the formulæ, the condition of maximum specific conductivity can be calculated, for since $\Lambda_M = \frac{\kappa}{\gamma}$, ($\gamma = \Gamma/1000$), the first equation can be written $\kappa = a\gamma + b\gamma^2$. The condition for maximum specific conductivity is therefore $a + 2b\gamma = 0$, or the concentration at which the

¹ *Ann. Chim. Phys.*, 1906, **7**, 289.

² *Trans. Roy. Soc. Edin.*, 1906, **45**, [i], 241.

maximum occurs is $-\frac{a}{2b}$ gram-equivalents per kilogram. This gave good agreement with the observed value in the case of sulphuric acid. It may be remarked that the adoption of the above mass units does not in any way affect the numerical statement of the relationships which have been established for dilute dilutions.

Chemical Activity and Electrolytic Conductivity.

The study of the connexion between chemical activity and electrolytic conductivity, begun by L. Kahlenberg in 1902, has been continued by J. L. Sammis,¹ who has studied the rate of inversion of cane-sugar, the catalysis of methyl acetate, and the solution of magnesium in solutions of nitric, hydrochloric, and acetic acids. In order to reduce the conductivity after the first measurements had been made, similar solutions were prepared in which an equal volume of benzene was substituted for part of the water present before. Where acetic acid was used, sufficient benzene could be added without forming two layers, and in the case of hydrochloric and nitric acids, aqueous acetone solutions were employed. It was found that in every case studied the substitution of benzene for part of the water produced changes in the rate of chemical action and in conductivity which were entirely out of proportion to each other, and were not always in the same direction.

The displacement of copper from non-conducting solutions of copper oleate by other metals was found to be more easily effected by lead than by sodium, magnesium, iron, zinc, or cadmium, although the latter metals are more electropositive than lead.

In connexion with the first part of the paper, reference may be made to determinations of the conductivity of nitric acid in water containing ether, carried out by P. Bogdan.² These show that although the ether scarcely affects the degree of ionisation, it greatly lowers the conductivity and therefore also the mobility of the ions.

Affinity Constants of Acids.

It has already been shown by Friedenthal and others³ that the actual concentration of hydrion and hydroxidion can be determined with accuracy by means of different indicators, and E. Salm⁴ has now shown how these can be employed for the determination of the degree of dissociation and dissociation constant of dibasic

¹ *J. Physical Chem.*, 1906, **10**, 593.

² *Zeit. Elektrochem.*, 1906, **12**, 489.

³ *Ann. Report*, 1904, 22.

⁴ *Zeit. Elektrochem.*, 1906, **12**, 99; *Zeit. physikal. Chem.*, 1906, **57**, 471.

acids, even in fairly concentrated solution. Thus the dissociation constants of oxalic, tartaric, fumaric, camphoric, and camphoronic acids were found to be 0.09, 0.0011, 0.0011, 0.000025, 0.000174 respectively, whilst the values found electrically by Ostwald were 0.1, 0.00097, 0.00093, 0.0000225, 0.000175.

Further, the dissociation constant of the indicator itself is equal to the concentration of the hydron or hydroxidion in the solution in which 50 per cent. of the indicator is dissociated. In the case of two-colour indicators this point is reached when the indicator shows its neutral tint; in the case of one-colour indicators, when the intensity of coloration is exactly half that of the fully dissociated solution. These points are determined colorimetrically. The concentration of hydron is then determined by measurements of electromotive force. The following values for the dissociation constants were obtained :

Acid indicators.	<i>K</i> .	Basic indicators.	<i>K</i> .
Methyl-orange	4.6×10^{-4}	Cyanine	4.2×10^{-6}
<i>p</i> -Nitrophenol	2.3×10^{-7}	Dimethylaminoazobenzene.	1.4×10^{-11}
Rosolic acid	1.1×10^{-8}		
Alizarin	8.8×10^{-9}		
Phenolphthalein	8.0×10^{-10}		

The application of indicators for the purpose of determining the concentration of hydron and for affinity measurements has also been made in a somewhat different manner by F. H. Eydman, jun.¹ On diluting the aqueous solution of an acid indicator with water, the colour approaches that of the anion, but if the dilution is carried out with an isohydric solution of a colourless acid, the colour remains constant. It is therefore possible to determine the dissociation constant of an acid indicator provided the dissociation constant of the colourless acid, the concentration of the solution, the amount of the colourless acid added, and the concentration of the acid indicator are known. Further, the dissociation of a colourless acid can be determined by preparing a solution of it isohydric with a standard solution of an acid the dissociation constant of which is known. The condition of isohydry is determined by means of the indicator.

If carbon dioxide is passed into the solution of the sodium salt of a weak acid, the amount absorbed is greater than by pure water, owing to the alkali produced by the hydrolysis of the salt. From the excess absorbed, the dissociation constant of the acid can be calculated, since that for carbonic acid is known. This method (due to Sand) has been applied by E. Bauer² for the determination of the dissociation constant of nitrous acid, the value found being 6.4×10^{-4} .

¹ *Rec. trav. chim.*, 1906, **25**, 83.

² *Zeit. physikal. Chem.*, 1906, **56**, 215.

Hydration of Ions.

With the object of throwing light on the question of the hydration of ions, G. Buchböck¹ electrolysed solutions of hydrochloric acid containing mannitol and resorcinol, and determined the changes in the relative concentrations at the two electrodes. His experiments go to show that water does indeed move with the ions. The ratio x/y , for the number of water molecules associated with hydron and chloridion respectively, diminishes with falling concentration of acid, and it seems probable that in infinitely dilute solutions the hydration of the chloridion is four times greater than that of the hydron.

Experiments of a similar kind have also been carried out by J. L. R. Morgan and C. W. Kanolt.² These investigators electrolysed solutions of silver nitrate in mixtures of pyridine and water, and of alcohol and water; also aqueous alcoholic solutions containing both silver nitrate and calcium nitrate. With silver nitrate in 52.75 per cent. alcohol the solvent undergoes no change, but with 66.24 per cent. alcohol change occurs showing that argention is united with water to the extent of 0.67—0.79 mol. of water to 1 mol. argention. With silver nitrate and calcium nitrate in 66 per cent. alcohol, the change in the composition of the solvent is very small, so that no definite conclusion could be drawn. In the case of silver nitrate in aqueous pyridine solution the pyridine wanders with the argention to the extent of 0.06—0.20 mol. of pyridine to 1 mol. argention.³

As an indication of the hydration of the ions, it has been pointed out by H. C. Jones⁴ that the greater the hydrating power of the electrolyte⁵ the greater is the temperature coefficient of the conductivity; that the temperature coefficients increase with the dilution, and that the increase is greatest for those substances which have great hydrating power.

No definite conclusion as to the hydration of solute molecules could be drawn by B. E. Moore⁶ from spectroscopic examination of solutions of copper and cobalt salts.⁷

From a consideration of anomalies in the solubility curves, J. J. van Laar⁸ concludes that it is the ions not the un-ionised molecules that are hydrated.

Non-aqueous Solutions of Electrolytes.

During the past year a considerable amount of work has been done, notably by P. Walden and by H. C. Jones and his co-workers on the conductivity and other physical properties of solutions of electrolytes

¹ *Zeit. physikal. Chem.*, 1906, **55**, 563.² *J. Amer. Chem. Soc.*, 1906, **28**, 572.³ Compare *Ann. Report*, 1904, 18.⁴ *Amer. Chem. J.*, 1906, **35**, 445.⁵ Compare *Ann. Report*, 1905, 24.⁶ *Zeit. physikal. Chem.*, 1906, **55**, 641.⁷ Compare G. N. Lewis, *ibid.*, 1906, **56**, 223.⁸ *Ibid.*, 1906, **54**, 750.

in non-aqueous solvents. Walden¹ has studied especially the solutions of tetraethylammonium iodide in organic solvents, and has arrived at the following main conclusions. The equivalent conductivity increases in most cases with dilution, as in aqueous solutions, but in some cases there are irregular variations which the author attributes to interaction between the solute and solvent. The author also finds, in confirmation of the Nernst-Thomson rule, that there is a close parallelism between the dielectric constant of the solvent and its ionising power for tetraethylammonium iodide; and the results obtained do not bear out the view that conductivity is determined by the association of the solvent molecules. For solutions in different solvents the expression $e \cdot \sqrt[3]{v} = \text{const.}$, where e is the dielectric constant of the solvent, and v the dilution at which, in that solvent, the degree of ionisation of tetraethylammonium iodide has a given value, is widely applicable; and it has been pointed out by E. Baur² that this is in harmony with a relationship previously put forward by him. Walden has also found that the product of Λ_{∞} and the temperature coefficient of conductivity is approximately constant, with a mean value of 1.30; so that from this the value of Λ_{∞} can be calculated.

With regard to the relation between viscosity and conductivity, Walden has found that solutions of tetraethylammonium iodide in dilutions greater than 200 have practically the same viscosity as the pure solvent, and that the temperature coefficients of viscosity and of conductivity are in the same order and often identical. It has further been found that $\eta_{\infty} \Lambda_{\infty} = \text{constant} = 0.700$ (where η_{∞} is the viscosity of the pure solvent), and this relationship is nearly independent of the temperature. This is in harmony with the view expressed by Kohlrausch that the ions are surrounded by an atmosphere of the solvent, so that the friction which they experience depends on the viscosity of the solvent.

With regard to the solvent power of different liquids, the author, regarding solution as a chemical process, shows that the solvent power (for tetraethylammonium iodide) increases as the dielectric constant and the association factor of the solvent increase; and that the limit of solubility is reached in different solvents when the degree of ionisation is the same. From this it also follows that the molecular conductivities of two saturated solutions are inversely proportional to the viscosities of the pure solvents.

H. C. Jones, E. C. Bingham, and L. McMaster³ communicate the results of a large number of measurements of the viscosity of mixtures of water with the alcohols and of acetone and alcohol, and of the con-

¹ *Zeit. physikal. Chem.*, 1906, **54**, 131; **55**, 207, 281, 688; also P. Walden and M. Centnerszwer, *ibid.*, **55**, 321.

² *Zeit. Elektrochem.*, 1906, **12**, 725.

³ *Zeit. physikal. Chem.*, 1906, **57**, 193, 257.

ductivity of various salts in solution in these solvent mixtures. In these cases also one finds, in general, a similar relation existing as was found by Walden (*supra*); but in certain cases, for example, lithium nitrate and calcium nitrate in solutions of acetone *plus* methyl or ethyl alcohol, the conductivity curve exhibits a maximum, although the fluidity curves of the mixtures are practically straight lines. To explain this, the authors assume a diminution of the solvent envelope surrounding the ions.

Reference may also be made to a paper by H. C. Jones, C. F. Lindsay, and C. G. Carroll,¹ in which they confirm an hypothesis previously put forward.²

G. N. Lewis and P. Wheeler³ have found that potassium iodide dissolves in liquid iodine with production of a conducting solution. The molecular conductivity of the solution increases linearly with the concentration to a maximum and then falls off. The authors give evidence in support of the thesis that the ionising power of a substance and the property of itself undergoing ionisation when dissolved in other substances go hand in hand; and they seek on the basis of this to explain the deviations from the Ostwald law of dilution exhibited by solutions of strong electrolytes.

In connexion with this, reference should be made to a paper by J. Timmermans⁴ in which he describes the use of iodine as a cryoscopic solvent. The molar weight of potassium iodide was found abnormally high, indicating polymerisation.

Amphoteric Electrolytes.

The change in the conductivity of water with the temperature involves the variation of the ionic concentration and the mobility of the hydrogen and hydroxyl ions with the temperature. The variation of the ionic concentration can be calculated by means of van't Hoff's thermodynamic formula from the heat of neutralisation of a strong acid by a strong base. This calculation has been carried out by J. Walker,⁵ who finds for the temperature coefficient of conductivity the expression $K = K_{18}(1 + 0.060T' + 0.0014T'^2)$, which agrees perfectly with the equation found experimentally by Kohlrausch. From this agreement one is justified in assuming that the hydrogen and hydroxyl ions and no other are responsible for the conductivity of pure water.

The experimental determination of the affinity constants of a considerable number of amphoteric electrolytes has been carried out during

¹ *Zeit. physikal. Chem.*, 1906, **56**, 129.

² *Ann. Report*, 1904, 16.

³ *Zeit. physikal. Chem.*, 1906, **56**, 179.

⁴ *J. Chim. phys.*, 1906, **4**, 170.

⁵ *Trans. Faraday Soc.*, 1906, **1**, 362.

the past year. Thus the affinity constants of the methyl derivatives of *p*-aminobenzoic acid and of glycine have been determined by J. Johnston¹; of the methyl derivatives of *o*- and *m*-aminobenzoic acids by A. C. Cumming²; the acidic constants of some ureides and uric acid derivatives, and the affinity constants of xanthine and its methyl derivatives, by J. K. Wood³; the affinity constants of histidine, arginine, and lysine, by A. Kanitz⁴; of *i*- β -asparagine, *o*-aminobenzoic acid, and acetoxime by H. Lunden.⁵ The work by Johnston and by Cumming has been discussed by J. Walker,⁶ who has also discussed some of the statements made by Lunden concerning the theory of amphoteric electrolytes.⁷

The conditions of equilibrium in solutions of an associated amphoteric electrolyte (for example, proteins) in the absence and also in the presence of other electrolytes, both ordinary and amphoteric, have been fully discussed by T. B. Robertson.⁸

Thermodynamics and Chemical Equilibrium.

Many attempts have been made⁹ to deduce interpolation formulæ for the temperature variation of chemical and physical equilibrium, and for the calculation of equilibrium from the ordinary data of thermochemistry, but until recently with only partial success. The problem has, however, been attacked and solved with essential success by Nernst.¹⁰

As is known, the equilibrium constant (*K*) of a reaction is connected with the heat of reaction (*Q*) by the van't Hoff formula, $Q = RT^2 \frac{d \log_e K}{dT}$, which, regarding *Q* as a temperature function, yields

on integration $\log_e K = - \frac{Q_0}{RT} + \frac{\sum \nu a}{R} \log_e T + \frac{\sum \nu \beta}{R} T + \dots + I$. Here, *Q*₀ is the heat of reaction at the absolute zero, ν is the number of molecules, and α , β , &c., are characteristic thermal constants for the participating substances. *I* is an unknown integration constant. Nernst now introduces the new assumption that the free energy (affinity) coincides with the total heat of reaction (change of total energy), not only at the absolute zero, but also throughout a range of temperature above that

¹ *Proc. Roy. Soc.*, 1906, **78**, *A*, 82.

² *Ibid.*, 103.

³ *Trans.*, 1906, **89**, 1831, 1839.

⁴ *Zeit. physiol. Chem.*, 1906, **47**, 476.

⁵ *Zeit. physikal. Chem.*, 1906, **54**, 532.

⁶ *Proc. Roy. Soc.*, 1906, **78**, *A*, 140.

⁷ *Ann. Report*, 1904, 19.

⁸ *J. Physical Chem.*, 1906, **10**, 524.

⁹ Compare *Ann. Report*, 1904, 9; 1905, 10.

¹⁰ *Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 1906, **1**, 1. See *Zeit. Elektrochem.*, 1906, **12**, 738; *Chem. Centr.*, 1906, ii, 397.

point. In the case of the vaporisation of a substance, the concentration of the saturated vapour (ξ) is given by the equation

$$\log_e \xi = -\frac{\lambda_0}{RT} + \frac{a - a_0}{R} \log_e T + \frac{\beta - \beta_0}{R} T + \dots + i$$

where λ_0 is the heat of condensation at the absolute zero. With the help of his new assumption, Nernst shows that the integration constant I of the chemical reaction is equal to $\sum \nu i$, that is, the unknown constant I , required for the calculation of the chemical equilibrium, is made up of the sum of constants which are characteristic of the substances taking part in the reaction, each of which can be determined by experiment.

Calculation of Vapour Pressure Curves.—For the calculation of the different values of i in the above equation, the variation of vapour pressure with temperature must be known. For this, van der Waals has given the equation $\log \pi/p = a(\tau/T - 1)$, where π and τ represent critical pressure and temperature. It is, however, shown by Nernst that a is not constant but increases with increase of molecular weight of the substance. An empirical formula has been found (see p. 6) which gives much better agreement, but for extrapolation over a wide range to absolute zero, Nernst deduces the expression

$$\log_e p = -\frac{\lambda_0}{RT} + \frac{3.5}{R} \log_e T - \frac{E}{R} T + i + \log_e R.$$

From this it is possible to calculate λ_0 and E from two values of λ and one value of p . Consequently, one can calculate the value of i or of the constant $C = \frac{i + \log_e R}{2.302}$, the so-called "chemical constant." The chemical constant has different values for different substances, but in most cases its value is in the neighbourhood of 3.

The above formula has been confirmed by O. Brill¹ from measurements of the vapour pressure of liquid ammonia.

Heat of Vaporisation.—From the formula just given for the vapour pressure, one obtains for the heat of vaporisation at the temperature $(T_1 + T_2)/2$, the expression

$$\lambda = R \frac{T_1 T_2}{T_1 - T_2} (1 - p/\pi) \log_e p_1/p_2.$$

From the values of λ at the boiling point, calculated for substances having very different boiling points, Nernst shows that Trouton's rule does not hold except over a restricted range of temperature. This has been confirmed by E. C. Bingham and by F. Henning (see p. 7).

¹ *Ann. Physik.*, 1906, [iv], 21, 170.

Equilibrium in Homogeneous Systems.—By referring the equilibrium constant to partial pressures of the reacting substances instead of to concentrations, a formula is deduced which allows of the calculation of equilibrium in gaseous systems. The formula has been applied to the calculation of the dissociation of water vapour and of carbon dioxide¹ at high temperatures, and good agreement found with the values determined experimentally by Nernst and von Wartenberg. The formula has also been successfully applied to the calculation of the electromotive force of the hydrogen-chlorine cell, and to the dissociation of ammonia.

Heterogeneous Equilibrium.—For the dissociation pressure of a solid into a gas and a solid, the approximate equation is obtained,

$$\log p = -\frac{Q}{4.571T} + 1.75 \log T + C,$$

where C is the chemical constant (*supra*). This equation gives satisfactory values when applied to the dissociation of sodium phosphate, calcium carbonate, and the ammonia metal chlorides.

The stability of chemical compounds at different temperatures, and the sublimation, melting point, and transition point equilibria are also discussed.

Temperature Variation of Reaction Velocity.

The law of change of reaction velocity with the temperature has hitherto been investigated over only a comparatively small range of temperature, but K. Jellinek² has now studied the velocity of decomposition of nitric oxide over the range 650—1750°. As a result he finds that the thermodynamic formula of van't Hoff, namely, $\log k = -A/T + B$, is unsatisfactory, but that the relationship $\log k = AT + B$, agrees fairly well with the experimental determinations. Since according to this formula, which applies to high temperatures, k would not become zero for $T=0$ (at absolute zero), the author adds the term $-C/T$, where C is a constant, so that the general form of the equation becomes $\log k = AT + B - C/T$.

From a knowledge of the values of k and a determination of the amount of nitric oxide formed when a mixture of detonating gas and air is exploded, the high temperature period of the explosion has been calculated to be of the order 10^{-4} second.

Adsorption.

The phenomena of adsorption have been studied by H. Freundlich,³ who has investigated the adsorption of a number of substances,

¹ *Ann. Report*, 1905, 13.

² *Zeit. anorg. Chem.*, 1906, 49, 2297.

³ *Zeit. physikal. Chem.*, 1906, 57, 385.

inorganic and organic, by charcoal. The author established, in the first place, the fact that in adsorption of dissolved substances by charcoal, we are dealing with a condition of true equilibrium, which, moreover, at a temperature of 25° , is attained with great rapidity. The equilibrium can be represented by the formula

$$\lambda = \frac{v}{m} \log_e \frac{a}{a-x} = a \left(\frac{a}{v} \right)^{-1},$$

where λ is a constant, independent of the amount of charcoal, v is the volume of the liquid, m the amount of charcoal, a the total amount of dissolved substance, x the amount adsorbed, and a and n are constants which depend on the temperature and the nature of the dissolved substance. This equation, however, does not hold for strongly dissociated substances, nor for substances which give rise to hydroxidion. Temperature has only a slight influence on the amount of adsorption.

The adsorption seems independent of the adsorbing substance, but depends on the solute and also on the solvent. Thus, in aqueous solutions, charcoal adsorbs inorganic salts and acids and substances containing a number of hydroxyl groups (for example, sugar) only to a very slight extent; aliphatic acids and aromatic acids, containing the sulpho-group, to a moderate extent; aromatic acids, chlorine, bromine, phenylthiocarbamide, &c., to a great extent. Again, certain substances which are readily adsorbed from water, sulphuric acid, or solutions of Glauber's salt are not or are only slightly adsorbed from organic solvents.

On the theoretical side, the author finds a suitable explanation of the phenomena of adsorption on the basis of the change of the surface tension between solid and liquid in accordance with the theorem of Gibbs, that substances which lower the surface tension must be adsorbed.

Among the consequences which follow from this is that from a solvent having a high surface tension a substance is all the more readily adsorbed the smaller its own surface tension is. It is also deduced that the marked increase in the surface concentration in dilute solutions is due to the fact that small amounts of dissolved substance exercise a relatively great effect on the surface tension.

The subject of adsorption has also been studied by W. M. Bayliss,¹ especially with regard to the adsorption of electrolytes by proteins. The general results are similar to those obtained by Freundlich, although the author finds that considerable time (about twenty-four hours at 25°) is required for the adsorption equilibrium to be reached. The action of electrolytes in facilitating or hindering the adsorption

¹ *Biochem. J.*, 1906, 1, 175.

of dyes was also studied, and it was found that the adsorption of dyes which form colloidal solutions is greatly affected by electrolytes; that in the case of electronegative dyes (for example, Congo-red) cations facilitate adsorption, anions hinder it, whilst the opposite holds for electropositive dyes. In both cases, however, the effect of the anions is very small compared with that of the cations. Further, the effect of bivalent cations is considerably greater than twice that of univalent ions. Salts of the heavy metals which form positively charged colloidal hydroxides in solution have a very powerful effect in promoting the adsorption of electronegative dyes. The explanation of the action of electrolytes and of electrically charged colloids is to be found in the negative charge assumed by non-conductors when immersed in water.

The adsorption of HCl , KCl , NaCl , BaCl_2 , CuSO_4 , by filter paper, has been investigated by P. N. Evans.¹

The adsorption and occlusion of carbon dioxide and of hydrogen by charcoal has been studied by M. W. Travers,² who regards the equilibrium as being determined by the diffusion of the gas into the charcoal, with gradually diminishing concentration towards the interior.³

Colloids.

Colloidal solutions in organic liquids of a large number of metals, including sodium, potassium, rubidium, and caesium, also of carbon, silicon, selenium, tellurium, sulphur, red phosphorus, Prussian-blue, &c., have been prepared by The Svedberg.⁴ The stability of the solutions is increased by the addition of a small quantity of a slightly dissociated electrolyte with a large positive ion of low mobility (for example, bromobenzene) and also by low temperature.

The average size of the particles in colloidal solutions of platinum, gold, and silver has been found by E. F. Burton⁵ to be $(2-6) \times 10^{-5}$ cm. The rate of migration of the particles of platinum, gold, silver, bismuth, lead, and iron in an electric field at 18° , for a fall of potential of 1 volt per cm. was found to be $(20.3, 21.6, 23.6, 11.0, 12.0, 19.0) \times 10^{-5}$ cm./sec. respectively, the particles of the first three metals moving towards the positive, those of the last three towards the negative pole. The value appears to vary inversely as the viscosity of the water when the temperature is altered.

The question of the precipitation of colloids by electrolytes continues to receive attention. E. F. Burton⁶ has found that when aluminium

¹ *J. Physical Chem.*, 1906, **10**, 290.

² *Proc. Roy. Soc.*, 1906, **78**, A, 9.

³ See also W. Vaubel, *J. pr. Chem.*, 1906, [ii], **74**, 232.

⁴ *Ber.*, 1906, **39**, 1705.

⁵ *Phil. Mag.*, 1906, [iv], **11**, 425.

⁶ *Ibid.*, 1906, [iv], **12**, 472.

sulphate is added to a colloidal solution of platinum or silver in increasing amounts, the electrical charge on the colloid first diminishes and then changes sign, and the point of maximum instability is found at the isoelectric point. The charge on a gram-equivalent of colloidal silver was found equal to 0.04, that for gold to be 0.12, of the charge corresponding to a gram-equivalent of a univalent ion.

B. H. Buxton, P. Schaffer, and O. Teague¹ have studied the precipitation not only of unorganised suspensions but also of bacteria. These authors consider that neutralisation of the charge is not in itself sufficient to account for the precipitation, but that adsorption and chemical combination probably also play (in some cases at least) an important part. The behaviour also of unorganised suspensions, normal bacteria, and agglutinin bacteria is not in all points the same, and the authors doubt if one theory can be obtained which will explain all cases.

N. Pappadà² considers that in the precipitation of hydrogels by electrolytes there is no chemical action, and he explains the precipitation as being due, not only to exchange of charges, but also to collisions.

When two colloids of opposite sign are mixed, precipitation takes place as a rule. J. L. des Bancel³ has now found that this precipitation is facilitated by certain non-electrolytes (for example, carbamide), but hindered by others (for example, ethyl alcohol, acetone).

H. Bechhold and J. Ziegler⁴ have studied the diffusibility of different substances in gelatin and agar-agar jellies, and find that the diffusibility is diminished as compared with aqueous solutions. Further, the presence of electrolytes and non-electrolytes alters the permeability of the jellies for other substances (for example, dyes), the permeability being diminished by sodium sulphate, glycerol, &c., but increased by carbamide. This action is brought into connexion with the diuretic action of carbamide.

In the case of diffusion of sodium chloride, ammonium chloride, and barium chloride in 10 per cent. gelatin solution, M. Yégounoff⁵ finds that the product of diffusion constant and velocity of diffusion is constant for equal molecular concentrations.

A review of the subject of colloids has been given by A. Lottermoser.⁶

¹ *Zeit. physikal. Chem.*, 1906, **57**, 47, 64, 76.

² *Gazzetta*, 1906, **36**, [ii], 259.

³ *Compt. rend.*, 1906, **143**, 174.

⁴ *Zeit. physikal. Chem.*, 1906, **56**, 105.

⁵ *Compt. rend.*, 1906, **142**, 954.

⁶ *Zeit. angew. Chem.*, 1906, **19**, 369.

Photochemistry and Spectroscopy.

The chlorination of benzene under the action of light has been investigated further by R. Luther and E. Goldberg,¹ who find that the reaction is retarded by the presence of oxygen. A solution of chlorine in benzene which has been completely freed from air is twenty times as sensitive to light as one which is in contact with air at the atmospheric pressure. The authors consider that this retarding action of oxygen explains what is called the induction period, which is met with in the case of a number of photochemical reactions (for example, combination of hydrogen and chlorine). Only after all the oxygen has been removed does the reaction velocity attain its maximum value. The phenomenon of "deduction" is probably due to the gradual collection of oxygen, either from the interaction of chlorine and water, or from the walls of the containing vessels. The fact that moist chlorine which has been exposed to light interacts more readily with hydrogen may be attributed to the removal of traces of oxygen during the preliminary exposure.

During the past year, not a little work has been done bearing on the relations between absorption spectra and chemical constitution.² The hypothesis that an absorption band appears whenever there is tautomeric change within the molecule had already been advanced by Baly and his co-workers,³ and had been successfully applied to several cases of keto-enolic tautomerism. During the past year this hypothesis has also been extended to account for the absorption band exhibited by α -diketones, the intramolecular change in this case being one involving the oxygen atoms. To distinguish this particular kind of oscillation from that involving a hydrogen atom, as in the case of keto-enolic compounds, the term *isorropesis* has been proposed. This hypothesis has been applied to a considerable number of diketones, and also extended to substances where isorropesis is supposed to occur between two nitrogen atoms or between a nitrogen and an oxygen atom. The authors also consider that colour and fluorescence are evidences of isorropesis.

A paper on fluorescence has been contributed by Gertrud Woker,⁴ in which it is shown that fluorescence can be diminished or destroyed by the addition of a complementary colour, or by the introduction into

¹ *Zeit. physikal. Chem.*, 1906, **56**, 43.

² A. W. Stewart and E. C. C. Baly, *Trans.*, 1906, **89**, 489; E. C. C. Baly and A. W. Stewart, *ibid.*, 502; E. C. C. Baly, W. H. Edwards, and A. W. Stewart, *ibid.*, 514; A. W. Stewart and E. C. C. Baly, *ibid.*, 618; E. C. C. Baly, Effie G. Marsden, and A. W. Stewart, *ibid.*, 966; E. C. C. Baly and W. B. Tuck, *ibid.*, 982; E. P. Hedley, *ibid.*, 730; C. K. Tinkler, *ibid.*, 856.

³ *Ann. Report*, 1905, p. 2.

⁴ *J. Physical Chem.*, 1906, **10**, 370.

the molecule of groups which shift the absorption bands towards the red-end of the spectrum. By the same means, invisible fluorescence (in the ultra-violet) can be rendered visible. Most effective in this connexion is the introduction of two phenyl nuclei in the ortho-position. Solvents also have an influence on the fluorescence, the greater the dispersion of the solvent, the less is the fluorescence, owing to the shifting of the absorption bands towards the red.

L. Francesconi and G. Bargellini¹ have also investigated a large number of organic substances with respect to fluorescence, and find that aliphatic compounds are non-fluorescent, whilst all aromatic compounds are actually or potentially fluorescent. The effect of the introduction of different groups is, in general, the same as that found by Woker.²

J. Stark³ has shown that canal-rays produce in an elementary gas both a line and a band spectrum, and that the line spectrum alone shows the Doppler effect. The line spectrum is due to the positive ions, whilst the band spectrum is due to the combination of the positive ions with the electrons.

Metastable State.

The results of a number of interesting experiments on the passage from the metastable to the labile state have been communicated by H. A. Miers and Florence Isaac.⁴ When a supersaturated solution of sodium nitrate, and various other salts, is allowed to cool and is at the same time kept in motion by stirring, crystallisation takes place at first gradually, but at a certain point there is a sudden formation of a shower of small crystals. In the case of solutions of different concentration, allowed to cool at different temperatures, the points at which the sudden crystallisation occurs lie on a curve, which is nearly parallel to the solubility curve. This curve, which the authors call the "supersolubility curve," represents the temperature and concentration of each solution when it passes from the metastable to the labile state. The temperature at which the shower of crystals appears depends somewhat on the conditions of the experiment; for example, rate of stirring. When supersaturated solutions were cooled in sealed tubes which were kept in motion, it was found that when the rate of cooling was slow, shower-crystallisation occurred at the temperature corresponding with the supersolubility curve.

The subject is also discussed by H. Hartley and N. G. Thomas,⁵ who have obtained results similar to those described.

With regard to the limit of supercooling of a liquid, H. A. Miers

¹ *Atti R. Accad. Lincei*, 1906, [v], 15, ii, 184.

² See also a paper by E. L. Nichols, *J. Franklin Inst.*, 1906, 162, 219.

³ *Phys. Zeit.*, 1906, 7, 355.

⁴ *Trans.*, 1906, 89, 413.

⁵ *Ibid.*, 1013.

and Florence Isaac have found that pure water contained in sealed tubes, and shaken, freezes spontaneously at -1.9° . When subjected to friction (for example, by glass, garnet, &c.), freezing occurred at -0.4° .

Enzyme and Enzyme-like Reactions.

The chemical dynamics of alcoholic fermentation by yeast has been studied by A. Slator,¹ who has sought to exclude complications by measuring the velocity of reaction (by determining the pressure of carbon dioxide evolved) only over a small range. The author found that the rate of fermentation of dextrose is proportional to the concentration of dextrose and almost independent of the concentration of sugar except in very dilute solutions. The temperature coefficient of the reaction was large (5.6 between 5° and 15°), but diminishes considerably with rise of temperature. The initial rates of fermentation of dextrose, lævulose, sucrose, and maltose are as $1:0.92:1.05:0.9$. The author considers that the reaction which is measured in these experiments is the slow decomposition of a compound of the enzyme and the sugar.²

H. Schade³ has studied the decomposition of sucrose in presence of alkalis. The brown colour usually developed in the solution is due to aldehyde resin and can be prevented either by hydrogen peroxide or by passing a current of gas through the solution. The decomposition of the sugar then occurs quite regularly, with formation of aldehyde and formic acid, and is a true hydroxidion catalysis. Further, in the presence of rhodium, the formic acid is decomposed into carbon dioxide and hydrogen, which in the nascent state reduces the aldehyde to alcohol. In this way one obtains an inorganic imitation of the ordinary alcoholic fermentation.

R. J. Caldwell⁴ has studied the sucroclastic action of acids as influenced by salts and non-electrolytes, the reaction being studied in weight-normal, instead of volume-normal, solutions. In this way it is found that the velocity of inversion increases only slightly with concentration. The effect produced by the addition of various substances is attributed by the author to a change in concentration owing to the hydration of the added substances, the concentrating action of sucrose and other carbohydrates being relatively small but distinct. From the effect produced by electrolytes, the author makes an estimation of the extent of hydration of the salts. The greater the solubility of the salt, the greater its hydration.

¹ *Trans.*, 1906, **89**, 128.

³ *Zeit. physikal. Chem.*, 1906, **57**, 1.

² See *Ann. Report*, 1905, 27.

⁴ *Proc. Roy. Soc.*, 1906, **78**, A, 272.

The catalytic acceleration of hydrolytic reactions by hydrion and hydroxidion is ascribed by P. Rohland¹ to the formation of undissociated water in the nascent state. The water is produced from the hydroxidion of water and the hydrion of the acid, or from the hydrion of the water and the hydroxidion of the base.

Reference may also be made to papers by G. Bredig,² H. P. Barendrecht,³ and R. O. Herzog.⁴

ALEX. FINDLAY.

¹ *Zeit. physikal. Chem.*, 1906, **56**, 319.

² *Zeit. Elektrochem.*, 1906, **12**, 581.

³ *Zeit. physikal. Chem.*, 1906, **54**, 367.

⁴ *Zeit. physiol. Chem.*, 1906, **48**, 365.

INORGANIC CHEMISTRY.

THE work done during the year in this department of chemistry is not dissimilar to that recorded in previous years; it reveals evidence of activity in a great number of directions, and from the circumstances of the case places on record the results of the examination of a great variety of materials. The revision of atomic weights and the refining of earlier observations continue still to attract workers prepared to use to the utmost advantage the facilities in the manipulation of gases, liquids, and solids, which are the accumulated heritage from the researches of the past century. The study of the rare elements, more especially of the rare earths, has contributed its quota to the year's work, still to leave the position of some elements in doubt and dispute. The construction of fusion diagrams largely employed in the investigation of alloys has been applied to the examination of the possibilities of combination in the case of other solid elementary bodies. The controversy as to the cause of the rusting of iron would appear to be closed by the investigations of Moody, who shows that carbon dioxide plays the important part in this chemical change. It is permissible to regard the discovery of a new gaseous oxide of carbon, referred to in a later section of this Report, as an addition to the facts of inorganic chemistry. The complex metalammonia compounds and the isomerism exhibited by these substances have, at the hands of Werner and others, received further extension and elucidation, and formed the subject of a special lecture given by Werner to the Berlin Chemical Society.

Revision of Atomic Weights.

Gray¹ and Guye² have, from a discussion of the results of the different determinations of the atomic weight of nitrogen, independently concluded that 14.010 may be accepted as the atomic weight of this element.

¹ *Ann. Report*, 1905, 35; also *Trans.*, 1906, 89, 1173.

² *Ber.*, 1906, 39, 1470, and *Arch. Sci. phys. nat.*, 1905, [iv], 20, 351, and Guye and Düvella, *Compt. rend.*, 1905, 141, 826.

Guye and Ter-Gazarian¹ have drawn attention to a source of error in fixing the atomic weight of silver in the potassium chloride which is always to be found even in the most carefully purified potassium chlorate, the amount varying from 0.022—0.029 per cent. Applying to Stas's results, a correction based upon this observation effects a reduction in the atomic weight of silver, to which the authors assign the value 107.89 ($O=16$).

Baxter² has redetermined the atomic weight of bromine, the mean of eighteen determinations of the ratio $Ag:AgBr$ giving a value of 79.953 for the atomic weight of bromine. From the conversion of silver bromide into silver chloride the value 79.952 for bromine is deduced ($Cl=35.473$). The mean of all Baxter's determinations gives 79.953, which is in agreement with Stas's determination, whereas Scott's results are somewhat lower. In this connexion, the determination of the density of chlorine gas may be mentioned. Treadwell and Christie³ give as the mean of two sets of determinations, representing five observations, the value 2.4885 ($air=1$), a value approximating to that found by Moissan and Binet du Jassoneix, namely, 2.490.

Baxter, in association with others, has published the results of the redetermination of the atomic weights of manganese,⁴ cobalt,⁵ and cadmium.⁶ The analysis of manganese bromide and chloride gives $Mn=54.96$, of cobalt chloride and bromide $Co=59$, and of cadmium bromide gives 112.467 for the atomic weight of cadmium. A more recent determination of the atomic weight of cobalt from the analysis of the chloride gives a mean value of 58.995.⁷

The analysis of strontium bromide according to Richards⁸ gives an atomic weight of 87.663 for strontium, and, if $Cl=35.473$ be accepted, from the chloride the value 87.661 is deduced; this result is in satisfactory agreement with that derived from the bromide, whereas if the older atomic weight of chlorine is employed the agreement is not so good. The author concludes that the mean of these two sets of determinations, namely, 87.662, may be accepted as the atomic weight ($O=16$).

The alternate oxidation and reduction of pure copper according to Murmann⁹ gives for the atomic weight of this element values varying from 63.573—64.153 ($O=16$); this variation, it is suggested, arises from the absorption of air by the porous copper. The atomic weight is estimated to be 63.53 with an error of ± 0.03 .

¹ *Compt. rend.*, 1906, **143**, 411.

² *Zeit. anorg. Chem.*, 1906, **50**, 389.

³ *Ibid.*, 1905, **47**, 446.

⁴ Baxter and Hines, *J. Amer. Chem. Soc.*, 1906, **28**, 1360.

⁵ Baxter and Coffin, *ibid.*, 1380.

⁶ Baxter, Hines, and Frevert, *ibid.*, 770.

⁷ Baxter and Coffin, *Zeit. anorg. Chem.*, 1906, **51**, 171.

⁸ Richards, *ibid.*, 1905, **47**, 145.

⁹ *Monatsh.*, 1906, **27**, 351.

Gutbier,¹ in conjunction with Birckenbach and Mehler, has by three different methods obtained values for the atomic weight of bismuth, the mean of which is 208.074.

The determination of the electrochemical equivalent of iodine made by Gallo² gives as a mean of twenty-four estimations the atomic weight 126.89 when silver is 107.93.

A new determination of the atomic weight of potassium is recorded by Richards and Stähler,³ who employed for this purpose specially purified potassium nitrate, which they subsequently converted into the chloride. The ratios $\text{KCl}:\text{AgCl}$ and $\text{KCl}:\text{Ag}$ were determined in the same manner as the ratios $\text{NaCl}:\text{AgCl}$ and $\text{NaCl}:\text{Ag}$ (see *Report*, 1905, 34). The results of eight experiments with three samples of potassium chloride gave for the ratio $\text{KCl}:\text{AgCl}$ an average of 0.520118:1. With five different samples of potassium chloride the average of nine experimental determinations of the ratio $\text{KCl}:\text{Ag}$ gave 0.691072:1. Taking the atomic weight of silver as 107.93 and that of chlorine as 35.473, the above results lead to 39.114 as the atomic weight of potassium.

Brill,⁴ experimenting with the micro-balance, has shown that Krüss's method of determining the atomic weights of the rare earths depending on the conversion of the acid sulphates into sulphates is not accurate, the temperature employed being too low. This conversion is complete at 450°, and at 700° a decomposition begins resulting in the formation of basic sulphates which is completed at 900°. The basic sulphates are completely transformed into the oxides at 1180°. The basic sulphates, $\text{M}_2\text{O}_3 \cdot \text{SO}_3$, of ytterbium, yttrium, erbium, lanthanum, and samarium have been prepared by this method. Judged by the temperature at which these basic sulphates begin to decompose, the basicity of the oxides of these elements increases in the following order: Yb, Er, Y, Sm, and La. Upon the results of this investigation Brill bases a method for the determination of the atomic weights of the elements of these rare earths. Feit and Przibylla⁵ show that a practical method of determining the atomic weights of these elements is to dissolve a known weight of the oxide in $N/2$ sulphuric acid and titrate back with $N/10$ caustic soda solution, using methyl-orange as indicator. In this way the following values for the atomic weights have been obtained: La = 139.17, Pr = 140.62, Nd = 144.6, Sm = 150.56, Eu = 152.66, Gd = 157.47, Yb = 173.52, Yt = 89.40. With the exception of europium and yttrium, the results are in good agreement with the most trustworthy of previous determinations.

¹ *Zeit. Elektrochem.*, 1905, **11**, 831.

² *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 24.

³ *Ber.*, 1906, **39**, 3611.

⁴ *Zeit. anorg. Chem.*, 1905, **47**, 464.

⁵ *Ibid.*, 1906, **50**, 249.

The conversion of dysprosium sulphate, $[\text{Dy}_2(\text{SO}_4)_3, 8\text{H}_2\text{O}]$ into the oxide (Dy_2O_3) has been employed by Urbain and Demenitroux to determine the atomic weight of the element. When the earth is prepared by the fractional crystallisation of the nitrate, the atomic weight found in this way is 162.52, whereas with the earth prepared by the fractional crystallisation of the ethyl sulphates the value 162.54 was obtained.¹ Hinrichsen and Sahlbom² have determined the atomic weight of tantalum by converting the metal into the pentoxide, which gives the value 181.0, somewhat lower than the atomic weight assigned to the metal by Marignac, whose method the authors consider to be faulty.

Rare Earths.

Matignon and Cazes³ find that samarium chloride (SmCl_3) is reduced to a lower chloride SmCl_2 , when heated at high temperatures in hydrogen or ammonia, or with aluminium powder. This chloride is a dark brown, crystalline powder, and is insoluble in carbon disulphide, benzene, chloroform, and the other organic solvents which dissolve the anhydrous chlorides of the rare metals. It is decomposed by water, forming samarium oxide (Sm_2O_3) and an oxy-chloride (SmOCl); hydrogen is also liberated. The chlorides of praseodymium and neodymium are not reduced; it is suggested that this difference may be employed in the separation of these elements. Samarium iodide⁴ is reduced to samarium iodide by heating in a current of hydrogen.

The dehydration of the hydrated chlorides of yttrium and ytterbium, $\text{YtCl}_3, 6\text{H}_2\text{O}$ and $\text{YbCl}_3, 6\text{H}_2\text{O}$, has been studied by Matignon,⁵ and the physical properties of the anhydrous chlorides so obtained described. The following compounds of neodymium have been isolated: $\text{NdCl}_3, \text{H}_2\text{O}$; $\text{NdCl}_3, 6\text{H}_2\text{O}$; $\text{NdCl}_3, 3\text{EtOH}$; $\text{NdCl}_3, 3\text{C}_5\text{NH}_5$; NdOCl ; NdBr_3 and NdI_3 , also $\text{NdH}_3(\text{SO}_4)_3$ and $\text{Nd}_2\text{O}_2(\text{SO}_4)$.⁶ Matignon and Traunoy⁷ describe a series of seven compounds, formed by the interaction of gaseous or liquid ammonia and anhydrous neodymium chloride; the temperatures of dissociation and heats of formation of these compounds have been determined. The determination of the heats of formation of the sulphates of lanthanum, praseodymium, neodymium, and samarium, made by the dissolution of the oxides in dilute sulphuric acid, shows the basic function of these oxides

¹ *Compt. rend.*, 1906, **143**, 598, and **142**, 785.

² *Ber.*, 1906, **39**, 2600.

³ *Compt. rend.*, 1906, **142**, 183.

⁴ Matignon and Cazes, *Ann. Chim. Phys.*, 1906, [viii], **8**, 417.

⁵ *Ann. Chim. Phys.*, 1906, [viii], **8**, 433 and 440.

⁶ *Ibid.*, 243.

⁷ *Compt. rend.*, 1906, **142**, 1042; see also *Ann. Report*, 1905, 37.

to decrease with increase in atomic weight.¹ For the preparation of pure cerium compounds the following method is recommended by Orloff.² The mixed sulphates are treated with ammonium oxalate; the precipitate formed consists of the oxalates of lanthanum, neodymium, praseodymium, yttrium, and some cerium, and from the filtrates containing the oxalates of thorium and cerium the latter slowly precipitates, whereas the former remains in solution. This separation is materially assisted by the addition of sodium sulphite to the solution.

A silicide of thorium, ThSi_2 , is formed by the interaction of the double fluoride of thorium and potassium and potassium silicofluoride and aluminium heated in an electric furnace at 1200° . This same compound is produced by heating thoria with silicon in an electric furnace, or by heating aluminium, silicon, and thorium together at 1000° .³ The compound ThAl_3 ⁴ is formed by the direct union of the elements when heated together in a vacuum, or by reducing potassium thorium fluoride or thoria with aluminium in an electric furnace. In appearance this alloy resembles aluminium; it is attacked by the halogens and mineral acids, but not by alkali solutions, whereas it is violently acted on by fused alkalis or carbonates of the alkali metals.

Eberhard,⁵ from a spectroscopic investigation of Urbain's⁶ preparations of terbium compounds, concludes that terbium is a well-defined element; according to Urbain,⁷ this element forms a sulphate of the composition $\text{Te}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, and has an atomic weight $159 \cdot 22$ ($\text{O} = 16$).

The evidence in support of the existence of the element victorium is still a matter of discussion, as is evidenced by the publications of Crookes,⁸ Urbain,⁹ and Marc.¹⁰

In conclusion, mention should be made of Urbain's *résumé* of his researches in this field of investigation made since 1899.¹¹

Attempts to prepare metallic thorium both by the action of sodium on the chloride and by electrolytic processes have not proved successful; the product was always found to contain some oxide (Moissan and Hönigschmid).¹²

The Argon Group.

The examination of the gaseous contents of forty-three thermal springs has revealed the general presence in these gases of argon and

¹ Matignon, *Compt. rend.*, 1906, **142**, 276.

² *Chem. Zeit.*, 1906, **30**, 733.

³ Hönigschmid, *Compt. rend.*, 1906, **142**, 157.

⁴ Hönigschmid, *ibid.*, 280.

⁵ *Sitzungsber. K. Acad. Wiss. Berlin*, 1906, 384.

⁶ *Ann. Report*, 1905, 37.

⁷ *Compt. rend.*, 1906, **142**, 957.

⁸ *Chem. News*, 1906, **43**, 143.

⁹ *Compt. rend.*, 1905, **141**, 954.

¹⁰ *Ber.*, 1906, **39**, 1392.

¹¹ *J. Chim. Phys.*, 1906, **4**, 31, 105.

¹² *Ann. Chim. Phys.*, 1906, [viii], **8**, 182.

helium, the proportion of which varies with the amount of nitrogen and indirectly with the amount of carbon dioxide. In the water of Mazières, the new gases formed 6.35 per cent. of the nitrogen¹ (Moureu).

Olszewski,² working with helium obtained from thorianite,³ has not been able to liquefy this gas, even when it is cooled by frozen hydrogen and submitted to a pressure of 180 atmospheres which was suddenly reduced to 1 atmosphere; in this way the temperature was lowered to -271.3° . The boiling point of helium is therefore estimated to be below -271° .

The density of the vapours of zinc, cadmium, mercury, sulphur, selenium, and arsenic has been determined in atmospheres of argon and of helium, and compared with the values obtained when atmospheres of nitrogen and of hydrogen are employed. From the results of these observations, Ternent Cooke⁴ concludes that these elements exhibit a tendency to unite with argon and helium. Scheerer (1844), in his analysis of malacone, a silicate of zirconium, entirely overlooked the small proportion of uranium which Kitchin and Winter-son⁵ find to be present in this mineral; further, these authors show that when this mineral is fused with potassium hydrogen sulphate a gas containing both argon and helium is given off.

Adopting the method used in previous reports, the results of investigations published during the year will be discussed under the headings of the several groups in the periodic system of the elements.

Group I A.

For the electrolytic preparation of lithium, Ruff and Johannsen⁶ recommend a mixture of bromide and chloride containing 13 per cent. of the latter; this mixture melts at 520° . A carbon anode and an iron cathode are employed and an *E.M.F.* of 10 volts and current of 100 amperes. The metal so obtained melts at 180° . Weyberg⁷ has obtained lithium aluminosilicates by fusing kaolin with lithium compounds. With the chloride and carbonate, the compound $\text{Li}_6\text{Al}_2\text{Si}_2\text{O}_{10}$ is formed, with the sulphate $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8$, whilst with the bromide $7\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot 2\text{LiBr}$ is produced. The hydroxides of lithium, rubidium, and caesium have been examined by Forcrand;⁸ each forms a monohydrate; the lithium compound, $\text{Li}(\text{OH})\text{H}_2\text{O}$, separates from its solutions in well-defined crystals which lose H_2O when heated, forming

¹ *Compt. rend.*, 1906, **142**, 1155.

³ *Ann. Report*, 1905, 38.

⁵ *Trans.*, 1906, **89**, 1568.

⁷ *Centr. Min.*, 1905, 646.

² *Bull. Acad. Sci. Cracow*, 1905, 407.

⁴ *Zeit. physikal. Chem.*, 1906, **55**, 537.

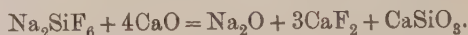
⁶ *Zeit. Elektrochem.*, 1906, **12**, 186.

⁸ *Compt. rend.*, 1906, **142**, 1252.

the hydroxide melting at 445° . The hydrated rubidium and caesium hydroxides, when dehydrated in silver crucibles, form peroxides which attack the silver. From solutions of lithium hydroxide and chromium trioxide in water at 30° , the substances separating in the solid state are $[\text{Li}(\text{OH})_2\text{H}_2\text{O}]$, $\text{Li}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Li}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, and CrO_3 . The solubility of the chromates of ammonium, potassium, sodium, and lithium increases in the order named, whilst for the dichromates the order is potassium, ammonium, lithium, and sodium.¹ Lebeau,² experimenting on the carbonates of the alkali metals heated in a current of carbon dioxide in an electric furnace, finds these carbonates to be non-volatile between 780° and 1200° , save in the case of caesium carbonate, which dissociates somewhat at 720° , a temperature much below that at which it volatilises.

The metalammonium compounds described by Joannis³ are, according to Ruff and Geisel,⁴ mixtures of metal with solutions of the metal in ammonia. These solutions decompose on keeping, with the evolution of hydrogen and the formation of metallic amides. Ruff and Geisel also show that the hydrides of the alkali metals are decomposed by liquid ammonia with the liberation of hydrogen and the production of amides. The oxidation of the solution of rubidium in ammonia yields a di- and tetra-oxide (Rb_2O_2 and Rb_2O_4), but no sesquioxide is formed as in the case with caesium (Rengade).⁵ The peroxide of caesium (Cs_2O_4) is formed when the metal is heated at $300\text{--}350^{\circ}$ in a stream of oxygen.⁶

The production of caustic soda by the decomposition of sodium silicofluoride with lime is the subject of a patent by Reich,⁷ who finds that the reaction is more complete when the amount of lime is double that required by the following equation :



The residue left after the removal of the alkali on dissolution in hydrochloric acid gives a solution of hydrogen silicofluoride which may be recovered as potassium silicofluoride. From solutions of sodium sulphate in sulphuric acid, two acid sulphates, namely, $\text{Na}_3\text{H}(\text{SO}_4)_2$ and $\text{Na}_3\text{H}(\text{SO}_4)_2\text{H}_2\text{O}$, have been obtained.⁸ The investigation of the fusion curves of mixtures of the haloids of potassium and sodium proves these salts to form isomorphous mixtures.⁹ According to van't Hoff

¹ Schreinemakers, *Chem. Weekblad.*, 1905, **2**, 633 ; see also *Zeit. physikal. Chem.*, 1906, **55**, 71.

² *Bull. Soc. chim.*, 1906, [iii], **35**, 5.

³ *Ann. Chim. Phys.*, 1906, [viii], **7**, 5.

⁴ *Ber.*, 1906, **39**, 828.

⁵ *Compt. rend.*, 1906, **142**, 1533 ; see also *Ann. Report*, 1905, 43.

⁶ Rengade, *ibid.*, 1149.

⁷ *D.R.-P.* 161795.

⁸ D'Ans, *Ber.*, 1906, **39**, 1534.

⁹ Kurnakoff and Schemtschuschny, *Chem. Centr.*, 1906, i, 526.

and Barschall,¹ glaserite is not a compound of the sulphates of potassium and sodium, but an isomorphous mixture of these sulphates. A study of the solid phases between iodine, an iodide, and polyiodide shows in the case of the alkali metals the tendency to form higher polyiodides to increase in the following order (LiNa), K, Rb, Cs, which is the order of decreasing solubilities of the platinichlorides (Abegg and Hamburger).²

When potassium is heated in a nickel dish, a black mass results, from which nickelous nickelite, $(\text{NiO}, \text{NiO}_2, 2\text{H}_2\text{O})$, has been obtained. The corresponding cobaltous cobaltite $(\text{CoO}, \text{CoO}_2, 2\text{H}_2\text{O})$ is formed by the action of potassium peroxide on cobaltous oxide.³

A simple process for the continuous production of potassium chlorate by the electrolysis of a solution of potassium chloride containing some potassium chromate and hydrochloric acid is described by A. Wallach.⁴

Wöhler and Kasarnowski⁵ consider the blue colour exhibited by some specimens of natural rock salt may be due to organic matter, as such specimens when heated in a current of oxygen were found to lose their colour and yield carbon dioxide and water. The colorations produced by heating halides with the metals probably arise from inclusion of the particles of the metals, or possibly from the production of sub-halides. The former explanation is supported by the ultra-microscopic examination of coloured specimens of rock salt made by Sidentopf.⁶

The investigations of the sulphides of rubidium and caesium by Biltz and Wilke-Dörfurt⁷ show the monosulphides $\text{Rb}_2\text{S}, 4\text{H}_2\text{O}$ and $\text{Cs}_2\text{S}, 4\text{H}_2\text{O}$ to be colourless, crystalline compounds, as are also the sulphydrates. From solutions of the monosulphides and sulphur the tetrasulphides $\text{Rb}_2\text{S}_4, 2\text{H}_2\text{O}$ and Cs_2S_4 have been obtained, the former in yellow crystals, the latter in reddish-yellow prisms. The pentasulphides (see *Annual Report*, 1905), when heated in a stream of hydrogen, lose sulphur and from the residue by dissolution in water the disulphides, $\text{Rb}_2\text{S}_2, \text{H}_2\text{O}$, $\text{Cs}_2\text{S}_2, \text{H}_2\text{O}$, are obtained in colourless crystals. When the pentasulphides are heated in a current of nitrogen the trisulphides $\text{Rb}_2\text{S}_3, \text{H}_2\text{O}$ and $\text{Cs}_2\text{S}_3, \text{H}_2\text{O}$ are obtained.⁸ The sulphides of rubidium are less hygroscopic than those of caesium, and Cs_2S_2 is more readily volatile than Rb_2S_2 .

Paal and Kühn⁹ record the formation of organosols and gels of sodium chloride and of sodium bromide by the addition of light petrol-

¹ *Zeit. physikal. Chem.*, 1906, **56**, 212.

² *Zeit. anorg. Chem.*, 1906, **50**, 403.

³ Hofmann and Hiendlmaier, *Ber.*, 1906, **39**, 3184.

⁴ *Zeit. Elektrochem.*, 1906, **12**, 667; see also Coppadoro, *Gazzetta*, 1906, **36**, ii, 321.

⁵ *Zeit. anorg. Chem.*, 1905, **47**, 353.

⁶ *Chem. Centr.*, 1906, i, 388.

⁷ *Zeit. anorg. Chem.*, 1906, **48**, 297.

⁸ *Ibid.*, 1906, **50**, 67.

⁹ *Ber.*, 1906, **39**, 2839 and 2863.

eum to the condensation product of ethyl chloroacetate or bromoacetate with ethyl sodiomalonate. When freshly prepared the precipitates are soluble in benzene, but become insoluble after drying in a vacuum. The gels so produced contain 58 per cent. or more of sodium chloride.

According to Mathewson¹ sodium forms a series of definite compounds with lead, cadmium, bismuth, and antimony.

Group I B.

The freezing point of pure copper is 1085°; it is depressed by cuprous oxide, the eutectic mixture solidifies at 1065° and contains, according to Dejean,² 4.7 per cent. of cuprous oxide which Heyn³ considers too high, and fixes the amount at 3.5 per cent. The maximum depression produced by aluminium is 1039°, corresponding to 8.6 per cent. of the metal. Moissan⁴ has succeeded in distilling copper in an electric furnace; the ingot left in the crucible on cooling exhibits the phenomenon of "spitting," and is covered by a layer of graphite.

Copper chloride heated in a vacuum with calcium turnings gives an orange-yellow, brittle alloy containing 18.3—18.8 per cent of copper.⁵ The chief product of the action of ammonia on heated cuprous oxide is the nitride Cu_3N , which is converted into cuprous chloride and ammonia by hydrochloric acid; it is attacked by nitric and sulphuric acids.⁶ Cuprosilicon, prepared by heating a mixture of these elements, consists in the main of the compound Cu_4Si and contains some free silicon in a form soluble in hydrofluoric acid⁷ (*Annual Report*, 1904, 45). The influence of small quantities of phosphorus, arsenic, antimony, bismuth, and lead on the structure of copper has been examined by Hiorns.⁸ Heyn and Bauer⁹ find that copper and cuprous sulphide are not perfectly miscible in the fused state, and that selenium and tellurium produce an alteration in the microstructure of copper similar to that produced by sulphur. The presence of these elements can be readily distinguished by treating copper turnings with a solution of potassium cyanide. On the addition of cadmium acetate dissolved in acetic acid, cuprous sulphide gives a yellow precipitate, whereas the selenide gives an orange; the telluride gives a coloration similar to that of permanganate on treatment with potassium cyanide. These

¹ *Zeñ. anorg. Chem.*, 1906, **50**, 171.

² *Rev. de Métallurgie*, 1906, **3**, 233.

³ *Ibid.*, 345.

⁴ *Compt. rend.*, 1905, **141**, 853.

⁵ Hackspill, *Compt. rend.*, 1906, **142**, 89.

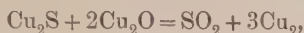
⁶ Guntz and Bassett, *Bull. Soc. chim.*, 1906, [iii], **35**, 201.

⁷ Lebeau, *Compt. rend.*, 1905, **141**, 889; 1906, **142**, 154; and Vigouroux, *ibid.* 1906, **142**, 87.

⁸ *J. Soc. Chem. Ind.*, 1906, **25**, 616.

⁹ *Métallurgie*, 1906, **3**, 73.

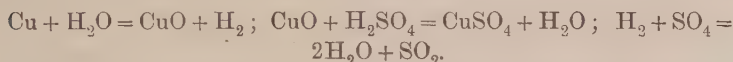
authors also state that sulphur dioxide does not attack copper at 900—1100°, save in presence of a reducing agent; and at this temperature the action of cuprous sulphide on cuprous oxide,



is complete.

From the freezing-point curves of mixtures of cuprous sulphide and ferrous sulphide Röntgen¹ infers the existence of the following compounds: $5\text{Cu}_2\text{S}, 2\text{FeS}$, $\text{Cu}_2\text{S}, \text{FeS}$, and $2\text{Cu}_2\text{S}, \text{FeS}$. The presence of metallic copper in copper mattes may arise from the change of Cu_2SFeS into Cu and FeS_2 .

The action of strong sulphuric acid on copper is maintained by Sluiter² to be best explained by the reduction theory, since these substances heated together at 130° with nitrobenzene yield aniline, whereas with sulphuric acid containing 12 per cent. of sulphur trioxide no aniline is formed. On the other hand, van Deventer³ considers neither explanation satisfactory, but suggests that water plays a part in the reaction, which he formulates as follows:



The alloys of copper and phosphorus have been investigated by Heyn and Bauer;⁴ these alloys are harder than the corresponding tin alloys, and a compound, Cu_3P , apparently exists. By employing higher pressures than the atmospheric pressure Friedrich⁵ has produced alloys of copper and arsenic containing as much as 44 per cent. of the latter element. The existence of several definite compounds are indicated by the melting-point curves of mixtures of these elements. Guillet⁶ has published an account of the examination of 'special brasses,' namely, copper and zinc alloys to which a third metal is added; whilst Pfeiffer⁷ concludes that copper does not alloy with iron or with iron and carbon alloys.

The production of colloidal copper oxide and of colloidal copper is described by Paal and Leuze.⁸

von Wartenberg's⁹ observations on the relative density of the vapour of silver at 2000° show the molecule to be mono-atomic, and that the metal volatilises at 1950°. The reduction of silver chloride by metallic calcium results in the formation of alloys containing from 6.3 to 16 per cent. of calcium; these alloys are grey, brittle, crystal-

¹ *Metallurgie*, 1906, **3**, 479.

² *Chem. Weekblad.*, 1906, **3**, 63.

³ *Ibid.*, 1906, **3**, 515.

⁴ *Mitt. K. Material-prüfungs Amt.*, 1906, **24**, 93.

⁵ *Metallurgie*, 1905, **2**, 477.

⁶ *Rev. de Métallurgie*, 1906, **3**, 243.

⁷ *Metallurgie*, 1906, **3**, 281.

⁸ *Ber.*, 1906, **39**, 1545 and 1550.

⁹ *Ibid.*, 1906, **39**, 381.

line solids, oxidised by the air and attacking water at the ordinary temperature.¹

That the electrolysis of a solution of silver nitrate gives a deposit of a black powder on the anode has been observed both by Watson² and Barbieri.³ The first of these authors shows this substance to be $\text{Ag}_7\text{NO}_{11}$, which is decomposed by boiling water, forming silver peroxide, thus:



and by ammonia with the formation of the oxide Ag_4O_3 , from the interaction of silver peroxide and ammonia:



Barbieri also records the observation that a layer of black oxide is formed on the anode when a solution of potassium hydrogen carbonate is electrolysed with silver electrodes; this deposit gradually dissolves to form a brown solution, which readily oxidises ferrous and cobaltous salts.

According to Lewis,⁴ silver suboxide is not formed by the decomposition of silver oxide Ag_2O , at 502° , 525° , or 445° .

The investigation of the action of silver nitrate on disodium hydrogen orthophosphate shows this reaction to take place in several stages; the silver phosphate contains only 76 per cent. of silver, whereas Ag_3PO_4 requires 77.32 per cent. Further, the solution always contains some phosphoric acid not precipitated by silver nitrate.⁵

The freezing-point curves of mixtures of silver with sulphur, selenium, or tellurium give no evidence of the existence of compounds other than Ag_2S , Ag_2Se , or Ag_2Te .⁶ The melting-point curves of mixtures of silver and silver sulphide have been examined by Friedrich and Leroux,⁷ who find that at 906° these substances separate into two layers, and from the eutectic mixture at 806° almost pure silver sulphide separates out. These authors from their investigation of the alloys of silver and arsenic fail to find any evidence in support of the existence of the compound Ag_3As ; by the reduction of silver arsenate with potassium cyanide at low temperatures they have obtained alloys containing 87.2—89.5 per cent. of arsenic.⁸

Silver and zinc appear to form compounds of the formulæ Ag_3Zn_2 , AgZn , Ag_2Zn_3 , and Ag_2Zn_5 ;⁹ with magnesium, silver forms alloys which are harder than either constituent; those rich in magnesium

¹ *Compt. rend.*, 1906, **142**, 89.

² *Trans.*, 1906, **89**, 578.

³ *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 500.

⁴ *J. Amer. Chem. Soc.*, 1906, **28**, 139.

⁵ Lang and Kaufmann, *ibid.*, 1905, **27**, 1515.

⁶ Pélabon, *Compt. rend.*, 1906, **143**, 294.

⁷ *Metallurgie*, 1906, **3**, 361.

⁸ *Ibid.*, 192.

⁹ Petrenko, *Zeit. anorg. Chem.*, 1906, **48**, 347.

are yellow, are readily oxidised, and decompose water more easily than magnesium.¹

Silver forms alloys with thallium, bismuth, and antimony; with the last only does it form a chemical compound, namely, Ag_3Sb .²

In connexion with their determination of the melting point of gold mentioned in last year's *Report*, Jaquero and Perrot³ give the following values for the coefficient of expansion of gases at temperatures ranging from 0° to 1067.4° : air 0.0036644, CO 0.0036638, O_2 0.0036652, and CO_2 0.0036756 and 0.0036713, that of nitrogen being 0.003664.

Ammonia unites with aurous iodide, forming $\text{AuI}\cdot 6\text{NH}_3$, which at 28° dissociates into $\text{AuI}\cdot \text{NH}_3$ and ammonia, and when heated forms ammonia, iodine, and gold; by water it is converted into ammonium iodide and gold. Aurous bromide forms $\text{AuBr}\cdot 2\text{NH}_3$, readily passing into $\text{AuBr}\cdot \text{NH}_3$; whereas aurous chloride forms $\text{AuCl}\cdot 2\text{NH}_3$, which, losing ammonia, gives $\text{AuCl}\cdot 3\text{NH}_3$; this compound is stable at 180° , but above this temperature is resolved into ammonium chloride and gold.⁴

Gold and zinc when alloyed appear to form the compounds AuZn , Au_3Zn_5 , AuZn_8 , and with cadmium gold forms Au_4Cd_3 and AuCd_3 ,⁵ whilst with antimony it forms the compound AuSb_2 , but no definite compound is obtained with bismuth.⁶ For the production of gold hydrosols the use of oil of turpentine (or pinene) or oil of rosemary is recommended by Vanino and Hartl,⁷ the colours produced depending on the temperature and concentration of the solutions.

Neumann⁸ has examined carefully the conditions required for the electrolytic precipitation of gold from cyanide solutions, using a lead or an iron cathode. The gold may also be deposited from these solutions using a carbon cathode, from which the gold may be stripped by using the gilded carbon as anode.

Group II A.

The analysis of a sample of electrolytic calcium from the Bitterfeld works shows it to contain some calcium carbide, iron, silica, and manganese, the last-named element being possibly derived from the steel tool used to break the calcium (Larsen).⁹ According to Doermer,¹⁰ calcium when strongly heated evolves hydrogen, which is reabsorbed

¹ Schemtschuschny, *Zeit. anorg. Chem.*, 1906, **49**, 400.

² Petrenko, *ibid.*, **50**, 133.

³ *Arch. Sci. Phys. Nat.*, 1905, [v], **20**, 506.

⁴ Meyer, *Compt. rend.*, 1906, **143**, 280.

⁵ Vogel, *Zeit. anorg. Chem.*, 1906, **48**, 319 and 333.

⁶ Vogel, *ibid.*, 1906, **50**, 145.

⁷ *Ber.*, 1906, **39**, 1696.

⁸ *Zeit. Elektrochem.*, 1906, **12**, 569.

⁹ *Chem. Centr.*, 1905, ii, 1466.

¹⁰ *Ber.*, 1906, **39**, 211.

at a lower temperature; when the metal is struck on an anvil explosions not infrequently occur. The dissolution of metallic calcium in molten cast-iron is attended by considerable development of heat, and some calcium carbide is formed. Whilst calcium reduces ferric oxide it does not combine with the iron produced; alloys of calcium with copper, aluminium, and magnesium are described by Stockem.¹ By the action of calcium on fused lead chloride alloys of lead and calcium are formed.² Calcium hydride is manufactured by heating electrolytic calcium contained in horizontal retorts in a current of hydrogen; the crude product contains 90 per cent. of the hydride, and may be used as a source of hydrogen; when decomposed by water one kilo. yields one cubic metre of the gas.³ Hoffmeister⁴ regards the colourless gas left after treatment of commercial acetylene with acetone and ammoniacal cuprous chloride as a gaseous hydride of calcium, for on burning in air it forms lime and water; with oxygen it forms an extremely explosive mixture. Attempts⁵ to prepare sub-salts of calcium by fusion of the metal with the chloride, iodide, or fluoride yield products which contain lime and calcium hydride, the latter resulting from the hydrogen produced by the action of the metal on the traces of water present. Commercial calcium peroxide is shown by von Foregger and Philipp⁶ to consist of calcium peroxide and calcium hydroxide, and to contain about 60 per cent. of the peroxide; when treated with water it forms calcium hydroxide and hydrogen peroxide. Calcium peroxide forms two hydrates, namely, $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ and $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$; the dry peroxide can be heated at 200° without change and is non-explosive. With respect to available oxygen it stands midway between neutral and acid calcium permanganate. The peroxides of strontium, magnesium, and zinc are decomposed at a lower temperature than the calcium compound. Tarugi's conception of the constitution of bleaching powder, referred to in the *Report* for 1905, p. 69, is refuted by Ditz,⁷ whilst Tiesenholt⁸ considers the view that bleaching powder is a mixture of calcium hypochlorite and calcium chloride to be supported by the observation that mixtures of calcium hypochlorite or lithium hypochlorite and calcium chloride are decomposed with the liberation of chlorine by moisture or carbon dioxide. Further, when bleaching powder is triturated with carbon tetrachloride it separates into two powders differing in their densities and chlorine content. The evolution of chlorine from aqueous solutions of bleaching powder is at-

¹ *Metallurgie*, 1906, **3**, 147; also Quasebert, *ibid.*, 28.

² Hackspill, *Compt. rend.*, 1906, **143**, 227.

³ Jaubert, *ibid.*, **142**, 788.

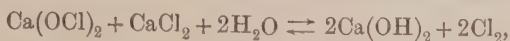
⁴ *Zeit. anorg. Chem.*, 1906, **48**, 137.

⁵ Guntz and Bassett, jun., *Bull. Soc. chim.*, 1906, [iii], **35**, 404.

⁶ *J. Soc. Chem. Ind.*, 1906, **25**, 298. ⁷ *Zeit. angew. Chem.*, 1905, **18**, 1690.

⁸ *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 834.

tributed to the hypochlorous acid formed by the hydrolysis of calcium hypochlorite, and the fact that calcium chloride more readily than other metallic chlorides brings about the following decomposition,



is considered to depend on the peculiar properties of its compounds with water of crystallisation.

Ammonium syngenite, $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, formed by adding calcium sulphate to a saturated solution of ammonium sulphate, is stable at 25° ; ¹ observations on the solubility of gypsum in ammonium sulphate ² and in magnesium sulphate ³ solutions are recorded.

By heating strontium hydride in a vacuum at 1000° , Guntz and Roederer ⁴ have obtained strontium as a silver-white metal, which tarnishes in the air and melts about 800° . It is attacked by water and alcohol; with carbon dioxide at a red heat it forms the carbonate and carbide. The authors have determined the heat of formation of $\text{SrCl}_2 \cdot \text{Aq}$ and of SrO , and obtain results some 11 Cals. higher than the values given by Thomsen. The electrolysis of an aqueous solution of strontium chloride using a mercury cathode yields two amalgams, one liquid and the other crystalline, of the composition SrHg_{11} ; the latter, when heated, gives Sr_2Hg_5 and SrHg_0 , and on distillation an amalgam distils over, so that metallic strontium cannot be obtained in this way. ⁵

The so-called strontium-ammonium decomposes slowly in a vacuum at 20° , leaving a residue of $\text{Sr}(\text{NH}_3)_2$; by the action of carbon monoxide strontium-ammonium is converted into $\text{Sr}(\text{CO})_2$, which becomes bright yellow when exposed to the air, and when heated forms strontia, strontium carbonate and carbon. Oxygen converts strontium-ammonium into strontia and the peroxide, whilst with nitric oxide it forms the hyponitrite. Hydrogen, nitrogen, and strontiamide are formed by the action of ammonia on the metal at 200° , and at 800° a mixture of nitride and hydride is produced. ⁶

Barium suboxide is formed by heating the oxide with magnesium in a vacuum at 1100° ; when heated together in the proportion of 3BaO to Mg an alloy distils over, but if aluminium is substituted for magnesium the distillate consists of metallic barium. ⁷ Bauer ⁸ has obtained a hydrated hydroxide of the formula $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$; strontium and calcium hydroxides do not form similar compounds. The behaviour of barium carbonate at high temperatures has been investi-

¹ D'Ans, *Ber.*, 1906, **39**, 3326.

² Bell and Taber, *J. physikal. Chem.*, 1906, **10**, 119.

³ Cameron and Bell, *ibid.*, 210.

⁴ *Compt. rend.*, 1906, **142**, 400.

⁵ Guntz and Roederer, *Bull. Soc. chim.*, 1906, [iii], **35**, 494.

⁶ Roederer, *ibid.*, 1906, iii, **35**, 715.

⁷ Guntz, *Compt. rend.*, 1906, **143**, 359.

⁸ *Zeit. anorg. Chem.*, 1905, **47**, 401.

gated independently by Finkelstein¹ and Boeke;² both find Le Chatelier's statement as to the fusion of barium carbonate to be erroneous; this compound does not melt at 1350°, but fuses partly when heated at 1380° in a stream of carbon dioxide. By prolonged heating at 1120° a basic carbonate is formed which dissolves baryta and at higher temperatures barium carbonate. Boeke finds that calcite is formed from aragonite at 470°, and that calcium carbonate does not melt even when heated to 1400—1500° in an atmosphere of carbon dioxide under pressure. The action of the alkali bromides on barium carbonate is observed by Taponier³ to increase with time, concentration, and temperature, and the following represents the order of decreasing activity: ammonium, sodium, and potassium bromides (*Annual Report*, 1905, 45). The solubility of barium sulphate in hydrogen peroxide solution has been established by Gawalowski.⁴ Neuberg and Neimann⁵ record some very interesting observations on the production of gelatinous modifications of salts of the alkaline earths; gelatinous barium sulphate, for example, is produced by treating the solution of barium oxide in methyl alcohol with dilute sulphuric acid. This jelly can be dried in a vacuum without change, but when boiled with water it becomes crystalline. Gelatinous barium carbonate is formed by the action of carbon dioxide in the methyl-alcoholic solution of the oxide, and this, if treated with more carbon dioxide, forms a white powder, $\text{BaCO}_3 \cdot \text{H}_2\text{O}$, which is soluble in water. A gelatinous sulphide, $\text{BaS} \cdot \text{H}_2\text{O}$, and gelatinous forms of other compounds are described. Vanino,⁶ continuing the study of phosphorescent sulphides referred to in last year's *Report*, finds that the sulphides of calcium and zinc do not emit Becquerel rays, and further, that whilst calcium sulphide loses its phosphorescence when suspended in water, it is not so affected by suspension in ether, acetone, ethyl, or amyl alcohol. The phosphorescence of these sulphides is shown by Jorissen and Ringer⁷ to depend on the presence of traces of salts of bismuth cadmium, and manganese, also of potassium and sodium chlorides, as the pure sulphides themselves are non-phosphorescent.

Group II B.

Glucinum hydroxide, heated alone or with water, or aqueous solutions of ammonia or alkali carbonate, or with alkali hydroxides, is gradually converted into a form sparingly soluble or insoluble in alkalis or

¹ *Ber.*, 1906, **39**, 1585.

² *Zeit. anorg. Chem.*, 1906, **50**, 244.

³ *Bull. Soc. chim.*, 1906, [iii], **35**, 280.

⁴ *Chem. Centr.*, 1906, ii, 7.

⁵ *Biochem. Zeit.*, 1906, **1**, 166.

⁶ *J. pr. Chem.*, 1906, [ii], **73**, 446; also *Ann. Report*, 1905, 45.

⁷ *Chem. Centr.*, 1906, i, 644.

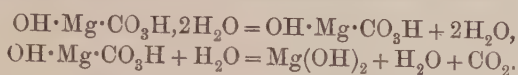
acids.¹ The conditions determining the existence of the hexa-, tetra- and di-hydrates of glucinum sulphate, and their solubilities, have been investigated by Levi-Malvano.² Davis³ shows that from the solution of magnesium carbonate in carbon dioxide and water crystals of the composition $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, separate out when the pressure of the carbon dioxide is reduced. This trihydrate is regarded as



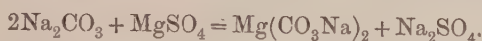
and its production explained by the equation,



When boiled with water, the trihydrate gives a mixture of magnesium hydroxide and the hydroxycarbonate, formed thus:



The addition of caustic soda to a solution of the bicarbonate does not produce a precipitate until boiled, because in the first instance the double salt, $\text{Mg}(\text{CO}_3\text{Na})_2$ (Deville, 1851, and Reynolds, *Trans.*, 1898, 73, 262), is formed, which on boiling is decomposed, forming a mixture of $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H} \cdot 2\text{H}_2\text{O}$, $\text{OH} \cdot \text{Mg} \cdot \text{CO}_3\text{H}$ and $\text{Mg}(\text{OH})_2$, which constitutes magnesia alba. The first stage in the production of magnesia alba is, therefore, the formation of the double sodium magnesium carbonate, thus:



The microscopic examination of magnesia alba shows it to be heterogeneous, as the above explanation would imply.

Zinc oxide heated in an electric furnace begins to volatilise at 1100° and does so rapidly at 1700° , the volatilised product exhibits well-defined crystalline structure. Cadmium oxide volatilises appreciably at 800° and readily at 1000° (Doeltz and Graumann).⁴

Precipitated zinc carbonate precipitates iron, aluminium, and uranium completely from cold solutions of ferric chloride, aluminium nitrate, and uranyl nitrate; but chromium is only partially precipitated from chromium nitrate solutions in the cold, and completely on boiling. Precipitated cadmium carbonate gives complete precipitations with solutions of ferric chloride and nitrate only.⁵

When cadmium is burnt at a low temperature, the product contains some peroxide (CdO_2).⁶

A modification of mercurous chloride, Meyer⁷ states, is produced by the reduction of mercuric chloride by lithium sulphite, which

¹ D.R.-P. 165488.

Atti R. Accad. Lincei, 1905, [v], 14, ii, 502.

² *J. Soc. Chem. Ind.*, 1906, 25, 788.

⁴ *Metallurgie*, 1906, 3, 212 and 372.

⁵ Kohn, *Zeit. anorg. Chem.*, 1906, 50, 315.

⁶ Manchot, *Ber.*, 1906, 39, 170.

⁷ *Zeit. anorg. Chem.*, 1905, 47, 399.

gives the ordinary calomel, in the filtrate from it the new form separates out in lustrous scales. From the study of the solutions of mercuric iodide in nitrobenzene, *m*- and *p*-nitrotoluene, and α -nitronaphthalene, it appears that the yellow modification only exists in these solutions.¹

By the interaction of solutions of mercuric chloride and borax two oxychlorides of mercury are formed, one crystallising in brown needles and the second in lustrous, golden scales.² By the action of iodine on mercurous sulphate, mercurous iodide, mercuric sulphate, and free sulphuric acid are formed. The action with mercuric sulphate does not take place so readily; in presence of water in excess the product consists of mercuric iodide and iodate; in presence of alcohol, sulphur trioxide is formed in addition and the alcohol is oxidised to acetaldehyde.³

Foote and Levy have investigated the double salts which the chlorides of potassium, rubidium, and sodium form with mercuric chloride.⁴ Duboin has extended his investigation⁵ of the compounds formed by mercuric iodide and the iodides of other metals, and has described the compounds containing the iodides of calcium, strontium, barium, zinc, cadmium, magnesium, and manganese.⁶

A number of investigations have been published during the year dealing with the alloys containing metals of this group. Sodium dissolves in magnesium to the extent of 2 per cent., forming an alloy melting at 638—650°, and magnesium dissolves in sodium to the extent of 1.6 per cent., forming a mixture which has the melting point of sodium. Zinc and sodium are only partially miscible; they form a compound which is either NaZn_{11} or NaZn_{12} .⁷ Magnesium appears to form definite crystalline compounds of the formulæ CdMg , Zn_2Mg , Bi_2Mg_3 , and Sb_2Mg_3 .⁸ The statement of Mönkemeyer⁹ that the compound ZnSb melts at 561° is not confirmed by Schemtschuschny,¹⁰ who finds that the compound breaks up at 537° into Zn_3Sb_2 and Sb , which, on cooling, form a stable system of ZnSb and Sb . Cadmium and copper form the compounds Cu_2Cd and Cu_2Cd_3 .¹¹ The freezing-point curves of zinc and arsenic do not afford definite information as to whether these elements form compounds or solid solutions.¹² The alkali and alkali earth metals, according to McPhail Smith,¹³ dissolve in mercury

¹ *Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 192.

² *Zeit. anorg. Chem.*, 1906, **49**, 336.

³ Brückner, *Monatsh.*, 1906, **27**, 341.

⁴ *Amer. Chem. J.*, 1906, **35**, 236.

⁵ *Ann. Report*, 1905, 46.

⁶ *Compt. rend.*, 1906, **142**, 40, 395, 573, 887, 1338, and **143**, 313.

⁷ Mathewson, *Zeit. anorg. Chem.*, 1906, **48**, 191.

⁸ Grube, *ibid.*, **49**, 72.

⁹ *Abstr.*, 1905, ii, 171.

¹⁰ *Chem. Centr.*, 1906, i, 536.

¹¹ Sahmen, *Zeit. anorg. Chem.*, 1906, **49**, 301.

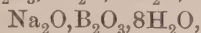
¹² Friedrich and Leroux, *Metallurgie*, 1906, **3**, 472.

¹³ *Amer. Chem. J.*, 1906, **36**, 124.

in the form of solutions of compounds of the formula MHg_m , whilst zinc, cadmium, bismuth, lead, and tin dissolve in mercury and do not form amalgams. The influence of small amounts of lead and of cadmium on the properties of zinc has been studied by Novak.¹

Group III A.

The mono-, di-, and penta-borates of potassium, sodium, and ammonium are described by Atterberg,² also barium monoborate and sesquiborate, $2BaO, 3B_2O_3, 7H_2O$; and Dukelski,³ from an investigation of the equilibrium at 30° in the systems (1) caustic potash, boric acid, and water, (2) caustic soda, boric acid, and water, concludes that solid borates of the following composition exist: $K_2O, B_2O_3, 2\frac{1}{2}H_2O$; $K_2O, 2B_2O_3, 4H_2O$, $K_2O, 5B_2O_3, 8H_2O$, $Na_2O, B_2O_3, 4H_2O$,

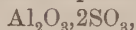


$Na_2O, 2B_2O_3, 10H_2O$, and $Na_2O, 5B_2O_3, 10H_2O$. Zinc and magnesium perborates are produced by the action of boric acid and sodium peroxide or of sodium perborate on zinc or magnesium salts; the zinc compound contains 9.5 per cent. of active oxygen, whilst the magnesium compound contains 11.9 per cent.⁴ Boron sulphide, B_2S_3 , is formed by passing hydrogen sulphide over powdered ferroboration heated at $300-400^\circ$, and condensing the product in a U-tube surrounded by ice.⁵ Ouvrard⁶ has prepared the chloroborates and bromoborates of strontium and barium similar to the calcium compounds mentioned in last year's *Report* (p. 46).

Silver ultramarine is formed by the action of silver nitrate and water on ultramarine at $110-180^\circ$; attempts to prepare ultramarine containing organic radicles such as ethylene, naphthyl, and triphenylmethyl have been unsuccessful.⁷ The blue colour observed by Knapp in his investigations of boron glass is due, as pointed out by Hoffmann,⁸ to the production of a boron-ultramarine by the action of sulphur on the sulphides present in the materials employed. Blue compounds are formed by heating mixtures of boron trioxide and borax in hydrogen sulphide or carbon disulphide.

Group III B.

A crystalline basic aluminium sulphate of the composition,



is manufactured by heating an excess of alumina with sulphuric acid

¹ *Zeit. anorg. Chem.*, 1905, **47**, 421.

² *Ibid.*, 1906, **48**, 367.

³ *Ibid.*, 1906, **50**, 38.

⁴ D.R.-P. 165278 and 165279.

⁵ Hoffmann, *Zeit. angew. Chem.*, 1906, **19**, 1362.

⁶ *Compt. rend.*, 1906, **142**, 281.

⁷ Chabrie and Levallois, *ibid.*, 1906, **143**, 222.

⁸ *Zeit. angew. Chem.*, 1906, **19**, 1089.

(s. g. 1.475); the solution after treatment with calcium carbonate or lime is evaporated under reduced pressure.¹ Although silicon and aluminium do not combine when heated together, yet in presence of the oxide or salt of another metal, compounds of silicon, aluminium, and the metal, so-called silico-aluminides, are formed. Several such silico-aluminides are described by Vigouroux;² they are metal-like, crystalline, hard and brittle substances; the majority resist the action of acids, except hydrofluoric acid, and are not attacked by solutions of the alkali hydroxides.

J. Meyer³ draws attention to sources of inaccuracy in the determination of the atomic weight of indium in the volatility of the oxide at high temperatures, and the incomplete decomposition of the nitrate even at 1100°.

By treatment of an alkaline solution of a thalious salt with hydrogen peroxide at low temperatures a dark brown, flocculent thallic oxide is formed, and at 80—100° it is produced as a black, heavy, sandy powder.⁴ The increase in weight observed when thallic oxide is heated over a bunsen burner arises from the formation of a mixture of normal and thalious sulphates, produced by the action of sulphur dioxide derived from the burning gas.⁵ Thomas⁶ has determined the heats of solution of the tetrahydrates of thallic chloride and thallic bromide, also of the chlorobromides, $\text{TiCl}_2\text{Br} \cdot 4\text{H}_2\text{O}$ and $\text{TiClBr}_2 \cdot 4\text{H}_2\text{O}$. Thalious chloride unites with chlorine at the temperature of liquid chlorine to form Ti_2Cl_3 , and at the ordinary temperature Ti_2Cl_4 is produced.

The aluminium alloys which Pécheux⁷ has shown to decompose water⁸ also precipitate copper from solutions of copper sulphate. Thallium is only partially miscible with copper at 954°; these metals form neither chemical compounds nor mixed crystals. Thallium behaves in a somewhat similar manner with aluminium;⁹ with antimony it is miscible in all proportions.¹⁰ Aluminium and tin do not combine chemically with one another; neither do aluminium and bismuth; further, the two latter metals are only slightly soluble in one another.¹¹

Group IV A.

A discovery of considerable interest and importance is that of a new gaseous oxide of carbon, which Diels and Wolf have found

¹ Spence, D.R.-P. 167419.

³ *Zeit. anorg. Chem.*, 1905, **47**, 281.

⁵ *Ibid.*, **50**, 158.

⁷ *Ibid.*, 575.

⁹ Doerincel, *Zeit. anorg. Chem.*, 1906, **48**, 185.

¹⁰ Williams, *ibid.*, **50**, 127.

² *Compt. rend.*, 1905, **141**, 951.

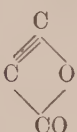
⁴ Rabe, *ibid.*, 1906, **48**, 427.

⁶ *Compt. rend.*, 1906, **142**, 838.

⁸ *Ann. Report*, 1905, 46.

¹¹ Gwyer, *ibid.*, **49**, 311.

amongst the products of the decomposition of ethyl malonate by phosphorus pentoxide at 300° .¹ Its composition is represented by the formula C_3O_2 ; it is combustible, burning with a blue, smoky flame to form carbon dioxide; by its reaction with water, ammonia, and hydrochloric acid, malonic acid, malonamide, and malonyl chloride are formed. To the name, carbon suboxide, proposed by its discoverers,¹ Berthelot² objects, as that name has been already appropriated for compounds discovered by Brodie in 1873, and examined by Berthelot himself. The constitutional formula $O:C:C:C:O$ has been assigned to this substance, but Michael³ considers it to be the lactone of

β -hydroxypropionic acid, for which the formula  is suggested.

The production of lamp black and graphite by the explosive decomposition of acetylene under a pressure of six atmospheres is described by Frank,⁴ who points out that the carbon resulting from the explosion of a mixture of acetylene and carbon monoxide or dioxide is entirely free from oily matters associated with the carbon obtained from acetylene alone. The carbon so produced is of higher electrical conductivity than ordinary charcoal, and forms a dense black pigment of high covering power. Calcium carbide heated in a current of carbon monoxide or dioxide yields graphite and lime; strontium and barium carbides behave similarly. Commercial calcium carbide contains graphite, representing carbon which has been dissolved by the fused carbide and separates out as graphite on cooling; the proportion of dissolved carbon depends on the intensity of the current used in the manufacture of the carbide.⁵ Manville⁶ has shown that the temperatures of formation of carbon monoxide and dioxide by the direct union of the elements are influenced by the form of the carbon and the velocity of the stream of oxygen. When a given form of carbon has been repeatedly heated in a vacuum and cooled, the temperature at which it reacts with oxygen is materially changed.

Pring and Hutton,⁷ investigating the action of carbon and hydrogen on one another at temperatures ranging from 1000° to 2800° , find that methane is produced at all temperatures, and that the production of acetylene begins at 1870° and continues up to 2800° . In these experiments the carbon rods were heated electrically and the temperatures estimated by the Wanner pyrometer. The reduction of

¹ Ber., 1906, **39**, 689.

³ Ber., 1906, **39**, 1915.

⁵ Kahn, *Compt. rend.*, 1906, **143**, 49.

⁷ *Trans.*, 1906, **89**, 1591.

² *Compt. rend.*, 1906, **142**, 533.

⁴ *Zeit. angew. Chem.*, 1905, **18**, 1733.

⁶ *Ibid.*, 1906, **142**, 1190 and 1523.

water vapour by carbon monoxide, according to Gautier,¹ takes place at 1200—1250°, and equilibrium is established when the volume of hydrogen is double that of the carbon monoxide, thus :



In this reaction traces of formic acid are produced. The reduction of carbon dioxide proceeds at 1300°, and the conditions of equilibrium are represented by the following equation :



These observations explain the presence in volcanic gases of carbon monoxide and dioxide, of water and hydrogen, also of formic acid. It has been observed by Farup² that carbon dioxide and water vapour react with equal velocity on carbon at 850°, whereas oxygen attains the same rate of reaction at 450°. When the diamond is heated in a porcelain tube in a current of carbon monoxide there is no reaction at 1000°, but at 1250° carbon is deposited on the porcelain but not on the diamond ; thus the catalytic action of the porcelain is greater than that of the diamond.

A carbide of boron, B_6C , is formed when petroleum coke and boron trioxide are heated together in an electric furnace ; the carbide, BC , previously described by Mühlhäuser, is probably a mixture of the carbide B_6C and graphite.³

By heating titanium containing some 2 per cent. of carbon in an electric furnace with a current of 1000 amperes at 55 volts, Moissan⁴ succeeded in distilling the metal. The distillate consists of minute crystals and contains some nitride. Iron, chromium, manganese, and tungsten can be distilled in the electric furnace, and from these experiments Moissan estimates the temperature of the sun to be nearer 2000—3000° than 6950°, as estimated by Wilson.⁵ Chloroform vapour passed over titanium dioxide heated in a hard glass tube gives the tetrachloride ; the action is a complex one ; titanium, titanium dichloride and trichloride are formed, also a colourless, gaseous hydride, TiH_4 . Tin tetrachloride but not silicon chloride can be obtained in a similar way.⁶ Titanium silicide, TiSi_2 , and the corresponding zirconium compound are formed by heating together powdered aluminium, sulphur, fine sand, and either titanous acid or potassium titanofluoride, or the corresponding zirconium compounds ; the mixture is covered with a layer of magnesium powder, and the action started by a Goldschmidt pastile.⁷ Valuable observations on the autoxidation

¹ *Compt. rend.*, 1906, **142**, 1382.

² *Zeit. anorg. Chem.*, 1906, **50**, 276.

³ *J. Amer. Chem. Soc.*, 1906, **28**, 605.

⁴ *Compt. rend.*, 1906, **142**, 673.

⁵ *Proc. Roy. Soc.*, 1902, **69**, 312.

⁶ Renz, *Ber.*, 1906, **39**, 249.

⁷ Hönigschmid, *Compt. rend.*, 1906, **143**, 224.

of tervalent titanium compounds have been made by Manchot and Richter.¹ Titanium trioxide shaken up with caustic potash and oxygen absorbs more than an equivalent of oxygen; hydrogen peroxide is formed first, and this converts the trioxide into titanium dioxide, or possibly into pertitanic acid. When baryta is substituted for caustic potash the hydrogen peroxide formed is retained as such.

Group IV B.

The temperature of formation of crystalline carborundum appears to be 1950° , and at 2220° it is decomposed into carbon and silicon.² Amongst the products formed by heating lime and coke together in an electric furnace a silicide of iron, FeSi , and also one of the composition FeSi_2 , have been obtained; the iron was derived from the coke.³ When solutions of sodium disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$) are decomposed by hydrochloric acid so as to form solutions containing 1 per cent. of silica, the silicic acid so produced exists in two modifications, an α - and β -form; the former is not precipitated by egg-albumin, and is converted into the latter by heat. Solutions of silicates of the types R_4SiO_4 , R_2SiO_3 , and $\text{R}_2\text{Si}_2\text{O}_5$ all yield solutions containing the α -silicic acid; solutions of water-glass yield the β -form in addition. The molecular weight of the α -modification is estimated at 155, whilst according to Sabanéeff the β -modification has a molecular weight of 49000.⁴ Observations on the melting points of silicates and of the rate of reaction in fused silicates have been published by Doelter;⁵ fused complex silicates form viscous masses from which crystallisation takes place very slowly; consequently the first to separate out from such a fused mass are the simpler silicates.

The electrolysis of an aqueous solution of stannous chloride containing some hydrochloric acid with two tin anodes on either side of a revolving copper cathode gives a deposit of spongy tin.⁶ The freezing-point curves of mixtures of tin and sulphur and of tin and selenium show that sulphur and selenium behave alike towards tin, which appears to form with sulphur SnS , Sn_2S_3 , and SnS_2 , whilst in the case of tellurium there is only one break in the curve, which corresponds to the production of a compound, SnTe .⁷ The solutions of orthostannic acid in sulphuric acid give with like solutions of calcium sulphate cubical crystals of the composition $\text{Sn}(\text{SO}_4)_2\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$.⁸ Similar compounds

¹ *Ber.*, 1906, **39**, 320 and 488.

² Tucker and Lampen, *J. Amer. Chem. Soc.*, 1906, **28**, 853.

³ Vanzetti, *Gazzetta*, 1906, **36**, i, 498.

⁴ Mylius and Groschuff, *Ber.*, 1906, **39**, 116.

⁵ *Zeit. Elektrochem.*, 1906, **12**, 413, and *Monatsh.*, 1906, **27**, 433.

⁶ Tommasi, *Compt. rend.*, 1906, **142**, 86.

⁷ Pélabon, *ibid.*, 1906, **142**, 1147.

⁸ Weinland and Kühl, *Ber.*, 1906, **39**, 2951.

are formed with the sulphates of strontium, barium, and lead; they are regarded as derivatives of a compound, $\text{Sn}[(\text{SO}_4\text{H})_3(\text{OH})_3]\text{M}''$, corresponding to the orthostannates of Bellucci and Parravano (see *Annual Reports*, 1904 and 1905).

By using a revolving cathode and low current density, lead can be deposited as an adherent metallic film from solutions of the acetate.¹ A yellow and red modification of lead monoxide are described by Ruer.² Lead peroxide is formed by the action of chlorine on a mixture of magnesia and lead sulphate suspended in water; the crude product is treated with caustic soda and then with nitric acid.³ Crystalline lead chromate (crocoite) is gradually deposited on exposing to air a solution of lead chromate in caustic soda; an alkaline solution of lead molybdate gives under similar conditions crystals of wulfenite.⁴ In the investigation of the freezing-point curves of mixtures of lead oxide and lead chloride the formation of $\text{PbCl}_2\cdot\text{PbO}$ (matlockite), $\text{PbCl}_2\cdot 2\text{PbO}$ (mendipite), and of $\text{PbCl}_2\cdot 4\text{PbO}$ is observed; it has also been noted that mixtures containing less than 88 per cent. of lead oxide may be fused in platinum vessels without attacking the platinum.⁵ The freezing-point curves of mixtures of galena and lead and the micrographical examination of the fused mixtures afford no evidence of the existence of Pb_2S or Pb_4S ;⁶ further, in a similar way, lead sulphide and iron sulphide when fused together are shown not to combine with one another.⁷ Alloys of lead and arsenic containing up to 34.4 per cent. of arsenic have been prepared by Friedrich;⁸ the investigation of these alloys affords no evidence of the existence of the compounds described by Descamps⁹ and Spring.¹⁰ Bock¹¹ has suggested that in the Pattinson process for the concentration of silver in lead, the iron of the vessels in which the metals are melted plays an important part in promoting a separation of the metals. This suggestion is shown by Friedrich¹² to be unfounded, as the separation is as perfect in porcelain as in iron vessels.

Group V A.

Erdmann¹³ describes an apparatus for the condensation of large quantities of nitrogen, which can now be obtained commercially pure;

¹ Snowden, *J. Physical Chem.*, 1906, **10**, 500.

² *Zeit. anorg. Chem.*, 1906, **50**, 265.

³ *Chem. Centr.*, 1906, ii, 465.

⁴ Cesáro, *Bull. Acad. Roy. Belg.*, 1905, 327.

⁵ *Zeit. anorg. Chem.*, 1906, **49**, 365.

⁶ Friedrich and Leroux, *Metallurgie*, 1905, **2**, 536.

⁷ Weidmann, *ibid.*, 1906, **3**, 660.

⁸ *Ibid.*, 41.

⁹ *Abstr.*, 1878, 705.

¹⁰ *Ibid.*, 1883, 650.

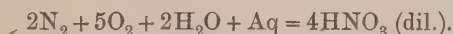
¹¹ *Chem. Zeit.*, 1905, **29**, 1149.

¹² *Metallurgie* 1906, **3**, 396.

¹³ *Ber.*, 1906, **39**, 1207.

dry oxygen is liquefied by cooling with liquid nitrogen, but not when cooled with liquid air. Ozone dissolves in liquid nitrogen, forming a blue solution. The production of oxidised products of nitrogen has engaged the attention of many workers. Schmidt and Böcker¹ find that when ammonia and air or oxygen are passed over platinum or platinised asbestos heated to redness, some 75 per cent. of the ammonia is oxidised to nitric oxide, which is subsequently converted into nitrogen trioxide. The products of the electrolysis of ammonia in presence of caustic soda are influenced by the nature of the anode employed: with platinum electrodes, sodium nitrate, a little nitrite, nitrogen and oxygen are formed; when the anode is either of copper, nickel, iron, or cobalt, sodium nitrite, nitrogen, and oxygen are alone produced.² The formation of nitrite has also been observed to take place when a solution of ammonia is electrolysed in presence of a copper salt and an alkali.³

The production of alkali nitrites by passing a mixture of air or oxygen and ammonia over heated metallic oxides is the subject of a patented process. With ferric oxide at 700° a continuous current of nitrous gas is obtained, which is converted into sodium nitrite by absorption in caustic soda.⁴ In discussing the fixation of atmospheric nitrogen, Guye⁵ points out that, whilst the yield of nitric oxide is raised by employing high temperatures, difficulties arise from the decomposition of this gas at such temperatures. The best effect is obtained when the gases are rapidly swept out of the region of the arc, or where a device is employed by which the arcs are rapidly lighted and interrupted several times a second, or again by causing the arc to play in different regions of the gases. The gases as they pass out of the vessels in which they have been submitted to the action of the electric arc contain from 1 to 2 per cent. by volume of nitric oxide, and on cooling to 500° or 600°, nitrogen peroxide and trioxide are formed which are absorbed by water. Under the influence of the silent electric discharge the nitrogen and oxygen of the air in presence of water or an alkali combine, forming nitric acid or nitrates, thus:



Neither nitrous acid nor ammonia is formed; the reaction is independent of the relative proportions of the two gases, and proceeds until the whole of the oxygen is used up (Berthelot).⁶ The oxidation of nitrogen by the passage of silent electric discharge through air has also been investigated by Warburg and Leithäuser.⁷

¹ *Ber.*, 1906, **39**, 1366.

² Müller and Spitzer, *Zeit. Elektrochem.*, 1905, **11**, 917.

³ Traube and Biltz, *Ber.*, 1906, **39**, 166.

⁵ *J. Soc. Chem. Ind.*, 1906, **25**, 567.

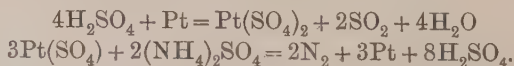
⁴ D.R.-P. 168272.

⁶ *Compt. rend.*, 1906, **142**, 1367.

⁷ *Ann. Physik.*, 1906, [iv], **20**, 743.

Kuriloff¹ concludes that the compounds of ammonia with metallic compounds are of three classes: (i) those of constant composition, in which the proportion of ammonia to the metallic compound is simple; (ii) those in which the composition is not constant, containing a variable amount of ammonia to one molecule of the metallic compound; (iii) colloidal class, in which there is no relationship between the ammonia and the metallic salts. The second class are analogous to hydrates, and the third class to hydrogels.

Raschig² describes a potassium hydroxylamineisodisulphonate ($\text{SO}_3\text{K} \cdot \text{NH} \cdot \text{O} \cdot \text{SO}_3\text{K}$), obtained from acid solutions of potassium hydroxylaminetrisulphonate, this compound is regarded as a derivative of the amide of Caro's acid, namely, $\text{H}_2\text{N} \cdot \text{O} \cdot \text{SO}_3\text{H}$. Ruff and Stäuber³ give a full account of their investigation of nitrosyl fluoride referred to in last year's *Report*. The chlorides of tin, antimony, and molybdenum react with nitrogen sulphide dissolved in chloroform, the additive compounds, $\text{SnCl}_4 \cdot 2\text{N}_4\text{S}_4$, $\text{SbCl}_5 \cdot \text{N}_4\text{S}_4$, and $\text{MoCl}_5 \cdot \text{N}_4\text{S}_4$, being formed; whereas the chlorides of titanium and tungsten are first reduced and then the reduced chlorides combine with the sulphide to form $\text{Ti}_2\text{Cl}_6 \cdot \text{N}_4\text{S}_4$ and $\text{WCl}_4 \cdot \text{N}_4\text{S}_4$.⁴ The action of liquid ammonia on solid nitrogen peroxide is one of great violence, but when moderated by passing ammonia gas over nitrogen peroxide at -20° , the products of the interaction are nitrogen, nitric oxide, water, ammonium nitrate, and a trace of nitrite. Nitrogen peroxide reacts slowly with ammonium chloride in the cold, but at 100° in sealed tubes the action is complete and results in the production of chlorine, nitrogen, nitrogen monoxide and trioxide, nitrosyl chloride, water, and nitric acid; ammonium nitrate and sulphate are also attacked by nitrogen peroxide.⁵ In connexion with the removal of nitrous acid from concentrated nitric or sulphuric acids, Silberrad and Smart⁶ find that carbamide, lead peroxide, oxamide, methylamine nitrate, or aminoguanidine nitrate react but slowly with nitrous acid in presence of these acids, whereas the action of hydrazine sulphate is very violent. Delépine⁷ draws attention to the possible error involved in the use of platinum wire or foil in the Kjeldahl process arising from the decomposition of ammonium sulphate, due to the following reactions:



The formation of nitric acid by the interaction of silver sulphate, ammonium persulphate, and dilute sulphuric acid is recorded by Kempf.⁸

¹ *Ann. Chim. Phys.*, 1906, [viii], 7, 568.

³ *Zeit. anorg. Chem.*, 1905, 47, 190, 192.

⁵ Besson and Rosset, *Compt. rend.*, 1906, 142, 653.

⁶ *J. Soc. Chem. Ind.*, 1906, 25, 156.

⁸ *Ber.*, 1906, 38, 3963.

² *Ber.*, 1906, 39, 245.

⁴ *Trans.*, 1906, 89, 1575.

⁷ *Compt. rend.*, 1905, 141, 886.

Group V B.

A convenient method of preparing phosphoric di-iodide is described by Doughty.¹ The conclusions drawn by Giran² as to the existence of various sulphides of phosphorus, based upon the behaviour on cooling of mixtures of these elements, are adversely criticised by Boulouch,³ who maintains that the trisulphide does not exist. Stock,⁴ in conjunction with others, has made a study of the action of liquid ammonia on phosphorus pentasulphide (see *Report*, 1905), an investigation which has resulted in the isolation of a number of phosphorus compounds. The additive product, $P_2S_5 \cdot 7NH_3$, is a mixture of ammonium iminotrithiophosphate, $P(SNH_4)_3 \cdot NH$, and ammonium nitrilodithiophosphate, $P(SNH_4)_2 \cdot N$. From the former, other salts of iminothiophosphoric acid, for example, $SH \cdot P(SNH_4)_2 \cdot NH$, have been prepared, and by the action of water on it ammonium thiophosphate, $PO(SNH_4)_3 \cdot H_2O$, is obtained. When heated at 180° in a vacuum, the ammonium iminothiophosphate gives thiophosphoric nitrile, $N:P:S$, which has also been produced by heating ammonium nitrilodithiophosphate at 300° in a vacuum. Many other derivatives of these compounds are described in the papers referred to.

Phosphorus chloronitride, PCl_2N , is the product of the interaction of phosphorus pentachloride and ammonium chloride; it is insoluble in water, but soluble in light petroleum and several organic solvents, and is dissolved by phosphorus oxychloride, sulphur dioxide, or nitrogen peroxide. A cryoscopic determination gives a molecular weight corresponding to the formula $(PCl_2N)_3$.⁵ From the measurements of the electrical conductivity, Parravano and Marini⁶ attribute to sodium hypophosphate the formula $Na_2H_2P_2O_6$, whilst Rosenheim, Stadler, and Jacobssohn⁷ from their determinations deduced the molecular formula $NaHPO_3$. From a mixture of a phosphate and sugar on treatment with sulphuric acid, the phosphorus can be completely vaporised by heat.⁸ Hydrogen phosphide is evolved from electrolytic ferrosilicon by treatment with water; the fatal cases of poisoning which have occurred on boats carrying ferrosilicon and the explosions in cargoes of this material in Liverpool in 1904 are to be attributed to the hydrogen phosphide formed in this way from ferrosilicon.⁹

The examination of the different methods for producing arsenic and sulphur compounds shows that only realgar and orpiment are produced, and that the pentasulphide, As_2S_5 , is not formed.¹⁰ Arsenic penta-

¹ *J. Amer. Chem. Soc.*, 1905, **27**, 1444.² *Compt. rend.*, 1906, **142**, 398.³ *Ibid.*, 1045, and **143**, 41.⁴ *Ber.*, 1906, **39**, 1967.⁵ Besson and Rosset, *Compt. rend.*, 1906, **143**, 37.⁶ *Atti R. Accad. Lincei*, [v], **15**, ii, 203.⁷ *Ber.*, 1906, **39**, 2857.⁸ *Ibid.*, 1906, **39**, 2625.⁹ *Zeit. Nahr. Genussm.*, 1906, **12**, 132.¹⁰ Borodowski, *Chem. Centr.*, 1906, ii, 297.

fluoride (AsF_5) is formed by the action of bromine and antimony pentafluoride on arsenic trifluoride. It is a colourless gas forming a yellow liquid at -50° and a white solid at -80° ; when dry, it does not attack glass, and when heated with silicon, arsenic and silicon fluoride¹ are produced.

A black and a yellow modification of antimony are produced by the action of oxygen on liquid antimony hydride at -40° and -90° respectively.² The selenide (Sb_2Se_3) and telluride (Sb_2Te_3) are formed by fusion of antimony with selenium or tellurium; these compounds form liquids when fused with either constituent, a property by which cryoscopic constant for antimony has been determined.³ Chrétien⁴ maintains that other selenides are formed, and gives 628° as the melting point of antimony.

Antimony sulphate, $\text{Sb}_2(\text{SO}_4)_3$, with water yields the basic salt, $(\text{SbO})_2\text{SO}_4$; with alcohol, the compound $\text{Sb}_2\text{O}_3 \cdot 2\text{SO}_3$ is formed. With alkali sulphates, double salts of the formula $\text{Sb}_2(\text{SO}_4)_3 \cdot \text{M}'_2\text{SO}_4$ are formed; the dissolution of antimony or antimony sulphide in sulphuric acid is greatly facilitated by the addition of an alkali sulphate.⁵ This last observation is applied in a patented process for the preparation of antimony oxide from antimony sulphide.⁶

The double compounds $\text{BiCl}_3 \cdot 2\text{KCl}$ and $\text{BiBr}_3 \cdot 2\text{KBr}$, also



are described by Aloy and Frébault.⁷ Gutbier and Bünz,⁸ investigating the so-called peroxides of bismuth, show that the product formed by the oxidation of bismuth oxide by chlorine in presence of an alkali is not a uniform material, nor is that which is formed by the oxidation with alkaline potassium ferricyanide as described by Hauser and Vanino (see *Report*, 1904); further, there is no evidence that these products possess acidic properties.

By the electrolytic reduction of vanadyl sulphate, vanadium hydrogen sulphate, $\text{Vd}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$, is formed; it gives double sulphates with those of rubidium and ammonium.⁹ Rutter¹⁰ finds that vanadic acid can be reduced electrolytically to vanadous sulphate by using a mercury cathode, and when a platinised platinum cathode is used the vanadic acid is reduced to a vanadic salt. Vanadous salts reduce silver bromide to metallic silver, and vanadic salts are oxidised by silver sulphate, a reaction assisted by copper sulphate, which is, how-

¹ Ruff, Graf, and Heller, *Ber.*, 1906, **39**, 67.

² Stock and Siebert, *ibid.*, 1905, **38**, 3837.

³ Pélabon, *Compt. rend.*, 1906, **142**, 207.

⁴ *Ibid.*, 1906, **142**, 1339 and 1412.

⁵ Metzl, *Zeit. anorg. Chem.*, 1906, **48**, 140.

⁶ D.R.-P., 161776.

⁷ *Bull. Soc. chim.*, 1906, iii, **35**, 346.

⁸ *Zeit. anorg. Chem.*, 1906, **45**, 162, 294; **49**, 432; and **50**, 210.

⁹ Stähler and Wirthwein, *Ber.*, 1905, **38**, 3978.

¹⁰ *Zeit. Elektrochem.*, 1906, **12**, 230.

ever, not reduced to metallic copper. The production of ammonium vanadate and sodium uranate from Utah sand, containing carnotite, is described by Ohly.¹

Double salts of columbium oxychloride and oxybromide of the types $\text{CbOCl}_3, \text{RCl}$ and $\text{CbOCl}_3, 2\text{RCl}$ are formed either by adding the halides to solutions of columbic acid in hydrochloric or hydrobromic acids, or by adding the halides dissolved in alcohol with hydrogen chloride or bromide to alcoholic solutions of the oxychloride or oxybromide of columbium. Cæsium, rubidium, quinoline, and pyridine compounds have been prepared.²

Group VI A.

Many workers have busied themselves with the study of the problems connected with the conversion of oxygen into ozone. Thus, Fischer and Braehmar³ have succeeded in demonstrating the formation of ozone and of nitrogen trioxide in the burning of hydrogen, carbon monoxide, acetylene, sulphur, and charcoal below or at the surface of liquid air. Ozone is also formed when platinum heated electrically to a white heat is submerged under liquid air or oxygen. Further, it has been observed that the production of ozone is favoured by rapid heating followed by rapid cooling, whereas the formation of nitric oxide takes place more readily when these conditions are reversed.⁴ As to the influence of the form of the electrode on the yield of ozone, Warburg and Leithäuser⁵ find that for small concentrations (4 grams of ozone per cubic metre) a highly positively charged sphere is the best, and for high concentrations (9 grams per cubic metre) a negatively charged sphere. Moisture reduces the yield of ozone, whereas a rise in temperature up to 80° has but little effect on the yield from oxygen, but produces a considerable reduction in the yield of ozone from air. Chassy⁶ has observed that with a given discharge reduction of pressure lowers the yield of ozone; observations on this subject are also recorded by Cermak.⁷ The formation of ozone in the electrolysis of solutions of hydrofluoric acid and of potassium fluoride described by Prideaux⁸ is easily explained in the light of the properties of fluorine.

The amount of ozone found by Lespieau⁹ in the air above the glaciers of Mont Blanc is 4.5 milligrams per 100 kilograms, and is shown to be independent of the altitude.

A redetermination of the density of ice made from water specially

¹ *Chem. Centr.*, 1906, ii, 165.

² Weinland and Storz, *Ber.*, 1906, **39**, 3056.

³ *Ber.*, 1906, **39**, 940.

⁴ *Ibid.*, 2557.

⁵ *Ann. Physik.*, iv, 1906, **20**, 734 and 751.

⁶ *Compt. rend.*, 1906, **143**, 220.

⁷ *Chem. Centr.*, 1906, ii, 585.

⁸ *Trans. Faraday Soc.*, 1906, **2**, 34.

⁹ *Bull. Soc. chim.*, 1906, [iii], **35**, 616.

freed from gases by boiling gives the value 0.91752, whereas Bunsen found it to be 0.9176.¹

Döring² finds that chromium, prepared by the aluminothermal method, containing some 97 per cent. of this element is less readily attacked by the halogen hydracids than those preparations containing a smaller proportion. Chromium can be electrolytically deposited from violet solutions of chrome alum, but not from the green solutions.³ The deposition of the metal from chromic salts is not necessarily preceded by the reduction to a chromous salt. Colson⁴ has extended his investigations of the sulphates of chromium referred to in last year's *Report*, and describes a green compound,



which is formed by reducing with sulphur dioxide a mixture of 2 molecular quantities of chromic acid and 3 molecular quantities of sulphuric acid dissolved in its own weight of water. A green chlorosulphate, $\text{CrClSO}_4(5\text{H}_2\text{O}), 3\text{H}_2\text{O}$, and a violet compound,



are described by Weinland and Krebs;⁵ the latter compound reacts with silver nitrate solutions, whilst the former does not. Bjerrum,⁶ does not agree with the conclusions of Weinland and Krebs as to the constitution of the chlorosulphates of chromium, for which in a later communication these authors have adopted different formulæ.⁷ It is only possible to refer to the researches of Werner and his pupils on the complex chromium compounds; the space at disposal in a Report of this kind does not suffice to do justice to the results of these important investigations,⁸ nor to Pfeiffer's⁹ discussion of the isomerism exhibited by complex chromium compounds. That solutions of chromium trioxide contain $\text{H}_2\text{Cr}_2\text{O}_7$ and H_2CrO_4 is supported by ebullioscopic and cryoscopic measurements, but no such evidence is forthcoming from electrical conductivity determinations.¹⁰ From experiments on the oxidising action of chromic acid and the results of the study of the action of dilute solutions of this substance on potassium iodide and hydrochloric acid, Seubert and Carstens¹¹ conclude that, as solutions of chromic acid contain $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions, also undissociated CrO_3 , it may be assumed that the reaction is represented as follows: $\text{CrO}_3 + \text{H}^+ + \text{I}^- = \text{CrO}_2\text{I}\cdot\text{OH}$, the complex $\text{CrO}_2\text{I}\cdot\text{OH}$ reacting with hydriodic acid to form iodine, water, and a chromic salt.

¹ Leduc, *Compt. rend.*, 1906, **142**, 149.

² *Zeit. Elektrochem.*, 1906, **12**, 329.

³ *Zeit. anorg. Chem.*, 1906, **48**, 251.

⁴ *Zeit. anorg. Chem.*, 1906, **49**, 157.

⁵ *Annalen*, 1906, **346**, 28.

⁶ *Zeit. anorg. Chem.*, 1906, **50**, 53.

⁷ *J. pr. Chem.*, 1906, [ii], **73**, 393.

⁸ *Compt. rend.*, 1906, **142**, 402.

⁹ *Ber.*, 1906, **39**, 1547.

¹⁰ *Ber.*, 1906, **39**, 329, 1823, 2656.

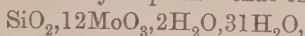
¹¹ Costa, *Gazzetta*, 1906, **36**, i, 535.

Alloys of molybdenum and boron are formed by the reduction of molybdenum dioxide heated with boron in magnesia crucibles. The alloys are non-crystalline, the hardness increasing with the percentage of boron; the highest proportion of boron found in these alloys being 46 per cent. These substances are not attacked by hydrochloric or hydrofluoric acids or alkalis, but are dissolved by dilute sulphuric and nitric acids, and are acted on by fluorine and chlorine at a red heat.¹ By heating together molybdenum and manganese at 1500° alloys are formed, and alloys richer in molybdenum are produced by reducing the mixed oxides with aluminium powder.² These alloys are silver white, non-magnetic, hard, brittle solids, consisting of mixtures of manganese with one or other of the compounds Mn_2Mo , MnMo , or MnMo_2 . Sodium silicomolybdate is formed by heating a mixture of sodium silicate and molybdic acid in the proportion



with a little water in sealed tubes at 150°. From the sodium salt a series of metallic silicomolybdates have been prepared, which are usually isomorphous with the corresponding silicotungstates. The crystals of potassium silicomolybdates and silicotungstates are optically active; dextro- and lævo-crystals have been obtained; the solutions are optically inactive.³

It has also been observed by Copaux⁴ that the acid



and the lithium salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{Li}_2\text{O}, 29\text{H}_2\text{O}$, form mixed crystals, and, further, that the acid, after the loss of $7\text{H}_2\text{O}$, forms mixed crystals with the barium salt, $\text{SiO}_2, 12\text{MoO}_3, 2\text{BaO}, 22\text{H}_2\text{O}$. The author concludes that isomorphism is dependent upon crystalline form rather than chemical composition.

The following compounds of iron and molybdenum, Fe_2Mo , Fe_3Mo_4 , FeMo , and FeMo_2 , have been isolated by Vigouroux⁵ from the product of the reduction of the mixed oxides by the Goldschmidt method, also by heating a mixture of the finely-divided metals in a stream of hydrogen.

Group VI B.

In the formation of polythionic acids by the interaction of sulphur dioxide and hydrogen sulphide, a hydrate of sulphur, $\text{S}_3\text{H}_2\text{O}$, is formed, and not a new allotropic form of sulphur, as suggested by Debus in 1888 (Spring).⁶ Sulphur heated in sealed tubes at 150—180° with aqueous solutions of cupric chloride reduces it to cuprous chloride, and under

¹ Arrivaut, *Compt. rend.*, 1906, **143**, 285.

² *Ibid.*, 464.

³ Copaux, *Ann. chim. phys.*, 1906, [viii], **7**, 118.

⁴ *Chem. Centr.*, 1906, i, 1673.

⁵ *Compt. rend.*, 1906, **142**, 889 and 928.

⁶ *Rec. trav. chim.*, 1906, **25**, 253.

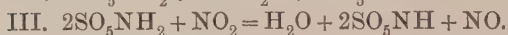
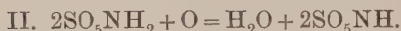
similar conditions reduces potassium dichromate to chromium sesquioxide.¹

The variations in the vapour pressures of mixtures of sulphur chloride (S_2Cl_2) and of chlorine, and of the boiling points also, confirm the existence of the dichloride SCl_2 , a conclusion supported also by dilatometric measurements.² Brückner³ finds that when anhydrous metallic sulphates are heated with sulphur in glass tubes through which the vapour of sulphur is passed, complex reactions take place, which in the case of the sulphates of the alkali metals and of the alkaline earth metals result in the production of sulphur dioxide, and a mixture of sulphide and thiosulphate of the metal. Magnesium, aluminium, and glucinum sulphate do not react with sulphur at a red heat; chromium sulphate gives a black Cr_2S_3 not attacked by hydrochloric acid; the sulphates of other metals yield sulphides and sulphur dioxide.

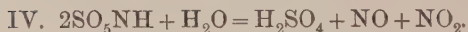
Lunge⁴ defends his theory of the lead-chamber process for the manufacture of sulphuric acid against the criticisms of Raschig, and maintains that the production of nitrous oxide and nitrogen by the action of sulphuric acid on nitrogen peroxide does not take place; further, that nitrogen trioxide is not an intermediate step in the conversion of nitric oxide to nitrogen peroxide. The following equations represent the changes taking place in the production of sulphuric acid.



The sulphonitronic acid is decomposed by oxygen or nitrogen peroxide, forming nitrosylsulphuric acid (SO_5NH).



The nitrosylsulphuric acid is then decomposed, thus:



The nitric oxide is finally oxidised to nitrogen tetroxide.

Examining the question of the loss of nitrogen in the lead-chamber process, Inglis⁵ finds that the reduction to nitrous oxide is very slight, and the chief source of loss of nitrogen compounds is the insufficient absorption in the Gay-Lussac tower. Selenium is found in the manufacture of sulphuric acid from pyrites containing this element in the elementary form, as selenious acid and as the compound $SeSO_3$, which dissolving in sulphuric acid imparts a green colour to the acid.

¹ *Atti R. Accad. Lincei*, 1906, [v], 15, i, 703.

² *Zeit. Physik.*, 1905, 54, 55.

³ *Monatsh.*, 1906, 27, 49.

⁴ *Zeit. anorg. Chem.*, 1906, 19, 807, 857, and 881.

⁵ *J. Soc. Chem. Ind.*, 1906, 25, 149.

Ten grams of selenium per ton of pyrites is sufficient to show itself in the process; the red sludge collecting in the Glover tower contains 2—4 per cent. of selenium. Littmann¹ concludes that the main quantity of selenium escaping from the pyrites exists as a labile volatile compound of a low stage of oxidation, possibly SeO , which is readily reduced to selenium or oxidised to selenium dioxide. Selenium can be readily detected in sulphuric acid by adding a crystal of potassium iodide to the diluted acid and removing the excess of iodine by sodium thiosulphate; selenium remains suspended in the solution, imparting to it a red coloration, changing to a lemon-yellow.

The most favourable conditions for the electrolytic production of thiosulphates from sulphite solutions have been investigated by Voghera,² who finds that the cathodic fluid should contain polysulphides rather than sulphides, the anode should be platinised platinum, the anodic solution a concentrated sulphite, faintly alkaline, and further a low anodic density should be maintained.

Price³ concludes that Caro's permonosulphuric acid is H_2SO_5 , not $\text{H}_2\text{S}_2\text{O}_9$, and is represented by the constitutional formula $\text{SO}_2\text{<}\begin{smallmatrix} \text{OH} \\ \text{O} \end{smallmatrix}\text{.OH}$, that of perdisulphuric acid being $\text{SO}_2\text{<}\begin{smallmatrix} \text{OH} & \text{HO} \\ \text{O} & \text{O} \end{smallmatrix}\text{>SO}_2$.

The statement that the reaction $\text{H}_2\text{S} + \text{ZnCl}_2 \rightleftharpoons \text{ZnS} + 2\text{HCl}$ may be displaced towards the right or the left by alteration of the external conditions has been examined by bringing the solutions into contact with hydrogen sulphide under a pressure of 14—16 atmospheres. Solutions of several metallic salts which under ordinary conditions give no precipitate gave precipitates when under pressure; whereas when the pressure is reduced by cooling the mixtures in solid carbon dioxide and ether, in no case did the precipitate dissolve, thus demonstrating that the reaction is not displaced to the left.⁴

Gautier⁵ finds that metallic sulphides are attacked by steam at temperatures varying from incipient redness to a white heat; sulphur dioxide, hydrogen, sulphur, and in some cases the metals themselves are formed. Hydrogen sulphide saturated with steam when passed through red-hot tubes gives sulphur dioxide, sulphuric acid, and colloidal sulphur. The presence of sulphur dioxide in volcanic gases is regarded by Gautier as due to the action of steam on metallic sulphides. The same authority has also studied the action of hydrogen sulphide on several oxides at high temperatures, showing that ferric oxide yields iron sulphide, alumina an oxysulphide, Al_2O_3 , Al_2S_3 , and silica a compound,

¹ *Zeit. angew. Chem.*, 1906, **19**, 1039.

² *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 363.

³ *Trans.*, 1906, **89**, 53.

⁴ Bruni and Padoa, *Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 525.

⁵ *Compt. rend.*, 1906, **142**, 1465 and **143**, 7.

SiO_2 , SiS_2 , whilst carbon dioxide and hydrogen sulphide passed together through a white-hot porcelain tube yield steam, hydrogen, carbon monoxide, sulphur, and carbonyl sulphide. The explanation of the presence of carbonyl sulphide in volcanic gases and in sulphur springs is to be found in this reaction.

For the isolation of selenium from sulphuric acid chamber residues the treatment with concentrated sulphuric acid at $50\text{--}60^\circ$, oxidation with solid potassium permanganate, and reduction with sulphur dioxide has been patented by Koch;¹ by heating amorphous selenium a metallic, crystalline, grey variety is formed, which exists as a labile and stable modification; both conduct electricity.² The reduction of selenious and selenic acids to selenium by organic compounds such as formic and oxalic acids, formaldehyde, benzaldehyde, dextrose, and others, has been observed by Oechsner de Coninck and Chauvenet.³ Oechsner de Coninck⁴ has also determined the solubility of selenium dioxide in several solvents; when treated with concentrated sulphuric acid, it yields SeSO_3 , hydrogen selenide and some amorphous selenium. Phosphorus pentachloride converts the dioxide into selenium tetrachloride (SeCl_4), whilst phosphorus trichloride gives brown amorphous selenium; both hydrazine and hydroxylamine hydrochloride reduce selenium dioxide, the former giving a black amorphous variety and the latter a red modification. The aqueous solution of the dioxide on exposure to light gives a deposit of selenium, insoluble in carbon disulphide.

Colloidal solutions of selenium and of sulphur can be obtained by electrolysing water with a cathode consisting of selenium or sulphur fused on to platinum foil; the selenium solution is fiery red, that of sulphur milky-white.⁵ With cathodes of this kind Le Blanc⁶ finds that in the electrolysis of solutions of caustic potash, polysulphides and polyselenides are formed, but these elements do not dissolve when employed as anodes. Tellurium, however, dissolves both as cathode and anode, in the first case to form polytellurides, and in the second it dissolves as Te^{+++} , the "ions" reacting to form TeO_3^{--} ions. At the cathode Te^{--} ions and at the anode Te^{+++} ions, in solutions the equilibrium between these ions is $3\text{Te} \rightleftharpoons 2\text{Te}^{--} + \text{Te}^{+++}$. The crystallography of the compounds TeBr_2Ph_2 and SeBr_2Ph_2 , also of the rubidium hydrogen selenate and tellurate, shows selenium and tellurium to be isomorphous, a conclusion supported by the study of the solidify-

¹ D.R.-P. 167457.

² Marc, *Ber.*, 1906, **39**, 697; also *Zeit. anorg. Chem.*, 1906, **50**, 446.

³ *Bull. Acad. Roy. Belg.*, 1906, 67 and 601.

⁴ *Compt. rend.*, 1906, **142**, 571.

⁵ Müller and Nowakowski, *Ber.*, 1905, **38**, 3779.

⁶ *Zeit. Elektrochem.*, 1905, **11**, 813, and 1906, **12**, 649.

ing points of mixtures of these elements in varying proportions (Pellini).¹

Group VII A.

Beyond what has already been referred to in the discussion of the other groups, there remains to mention Doerinkel's² study of the freezing-point curves of mixtures of manganese and silicon, which indicate the existence of the compounds Mn_2Si , $MnSi$, and $MnSi_2$, conclusions which confirm the observations of Lebeau based on the results of the action of different solvents on alloys of manganese and silicon.

Group VII B.

Fluorine dissolves in liquid chlorine, but reacts with chlorine water, producing hydrofluoric and hypochlorous acids (Lebeau).³ Deussen,⁴ continuing the examination of the properties of hydrofluoric acid, referred to in last year's *Report* (p. 59), finds the constant boiling solution of this compound in water has a boiling point of 111° at 750 mm. and contains 43.2 per cent. of hydrogen fluoride.

Attention is drawn by Fabinyi and Förster⁵ to differences in colour, solubility in water, and reactivity with hydrogen of chlorine prepared by allowing sulphuric acid to drop on to a mixture of potassium dichromate and salt, and of chlorine obtained by adding salt to a mixture of potassium dichromate and sulphuric acid. This difference, especially the greater activity of chlorine prepared by the second method, it is suggested, may be explained by assuming the chlorine atoms to be constituted of a different number of electrons. The function of the catalyst in the Deacon process for the manufacture of chlorine appears to be in part catalytic and in some degree chemical, and dependent on the formation of unstable hydrates by the catalyst.⁶ Liquid chlorine can be usefully employed in the preparation of iodine trichloride by causing it to react on iodine or metallic iodides; with bromine it forms both the mono- and tri-chloride, according to the proportions employed. Sulphur is not acted on by liquid chlorine, but the di- and tetra-chlorides of selenium are formed by its action on selenium; arsenic is converted into the trichloride, but antimony and bismuth are not attacked. Liquid chlorine, further, converts thallous into thallic chloride, but is without action on carbon disulphide, lead and manganese chlorides, or potassium permanganate.⁷

From an elaborate and thorough investigation of the interaction of

¹ *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 629 and 711; ii, 46.

² *Zeit. anorg. Chem.*, 1906, **50**, 117.

³ *Compt. rend.*, 1906, **143**, 425.

⁴ *Zeit. anorg. Chem.*, 1906, **49**, 297.

⁵ *Chem. Centr.*, 1906, i, 636.

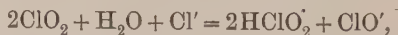
⁶ Levi and Voghera, *Gazzetta*, 1906, **36**, i, 513; *Ann. Report*, 1905, 59.

⁷ Thomas and Dupuis, *Compt. rend.*, 1906, **143**, 282.

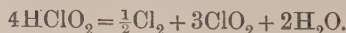
chlorine and hydrogen Burgess and Chapman¹ conclude that there is no evidence of a photochemical induction with moist chlorine and hydrogen, in the absence of impurities which are capable of destruction under the conditions of experiment. The photochemical induction noted by other experimenters is attributed by the authors to the presence of traces of ammonia or of compounds yielding ammonia. It is also maintained that there is no sufficient evidence to justify the view that the action of these elements is contributed to by the formation of condensation nuclei. The action of light in causing the union of chlorine and hydrogen appears to be due to the light absorbed by the chlorine becoming degraded into heat, and in this degradation a form of chemically active energy is produced. A method for the preparation of hydrogen chloride and bromide has been patented by Hoppe;² this method depends on the hydrolysis of certain metallic chlorides resulting in the formation of the hydracid and a basic salt of the metal, which is then converted into the corresponding halide by suspending it in water and treating it with a mixture of hydrogen and the halogen (chlorine or bromine); thus from the basic zinc chloride the normal chloride is regenerated in accordance with the equation:



Bray³ has published several papers dealing with the oxyhalogen compounds, and especially with the reactions of chlorine peroxide and chlorous acid. From the study of the oxidation of an iodide by potassium permanganate, hypochlorous acid, ozone, hydrogen peroxide, iodic acid, potassium persulphate,⁴ and arsenic acid, it is concluded that in all cases of oxidising agents containing oxygen the first product is hypiodous acid or a hypiodite, and probably similar compounds are formed in the oxidation of other halogens. The cryoscopic examination of aqueous solutions of chlorine peroxide indicate that this substance forms a hydrate, $\text{ClO}_2 \cdot 8\text{H}_2\text{O} (\pm \text{H}_2\text{O})$, analogous to chlorine hydrate; like chlorine, it forms a compound with water and carbon tetrachloride. In the reduction of chlorine peroxide a chlorite is a primary product; the reaction may be represented thus:



the chlorous acid further decomposing into chloric acid and hydrochloric acid, also into chlorine and chlorine peroxide, thus:



¹ *Trans.*, 1906, **89**, 1399.

² D.R.-P. 166598.

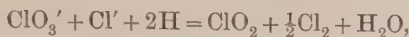
³ *Zeit. physikal. Chem.*, 1906, **54**, 463, 569, and 731; also *Zeit. anorg. Chem.*, 1906, **48**, 217.

⁴ See also Merk, *Chem. Centr.*, 1906, **i**, 397.

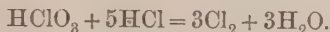
The study of the reactions of chlorine peroxide shows that in the dark with water it forms chloric acid and hydrochloric acid :



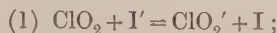
This action is assisted by the presence of chlorine ions and by metallic platinum, but not by chlorate ions. In alkaline solutions a mixture of chlorate and chlorite is formed. Chloric acid and hydrochloric acid,¹ when the concentration of chlorine ions is small, react as follows :



whereas with relatively concentrated hydrochloric acid the reaction proceeds thus :



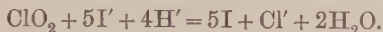
The action of chlorine peroxide on iodides in solutions of alkali hydrogen carbonates saturated with carbon dioxide is :



in neutral solutions the following change takes place :



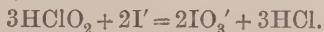
whereas in acid solutions the reaction is represented by the equation :



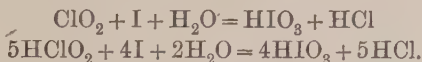
In all cases the first action results in the production of hypiodous ions, which reacting with iodine and hydrogen ions give free iodine and water, thus :



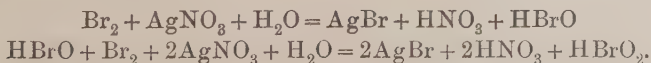
In presence of a large proportion of acid, then, reaction (1) is followed by the action of chlorous acid on iodine ions, forming iodic acid and hydrochloric acid :



The oxidation of iodine to iodate takes place in the following reactions :



Bromous acid² is formed when bromine is added to saturated solution of silver nitrate ; the formation is probably dependent on the following reactions :



¹ See also Luther and MacDougall, *Zeit. physikal. Chem.*, 1906, 55, 477.

² Richards, *J. Soc. Chem. Ind.*, 1906, 25, 4.

For the preparation of aqueous solutions of hydriodic acid, Bodroux¹ recommends a convenient method, depending on the action of barium peroxide on iodine, then removing the excess of iodine by sulphur dioxide, and at the same time converting the barium into the sulphate, the filtrate from which contains the hydriodic acid, and can be concentrated in the usual way.

Group VIII.

The volatility of iron is established by Moissan,² who has succeeded in distilling this and several other metals by heating them in an electric furnace, and in this manner obtaining crystalline distillates. The metals nearly allied to iron decrease in volatility in the following order: manganese, nickel, chromium, iron, uranium, molybdenum, and tungsten. Further, Moissan also finds that the metals indium, osmium, palladium, platinum, rhodium, and ruthenium, when heated in carbon crucibles in an electric arc produced by 500—700 amperes at 110 volts, are all fused and boil, giving distillates consisting of spherules or microscopic crystals. Palladium melts more readily than platinum, whilst of these metals osmium is the most difficult to distil.³ In the last *Report* mention was made of the researches of Dunstan, Jowett, and Goulding on the rusting of iron, of which phenomenon Moody⁴ gives the following explanation. The rusting is due to the influence of carbon dioxide; neither water nor oxygen free from this gas has the slightest effect. A trace of carbon dioxide suffices to start the action, and freshly formed rust always contains some ferrous carbonate, which is readily attacked by oxygen. Hydrogen peroxide when pure and free from acid has no action on metallic iron. These conclusions are supported by satisfactory experimental evidence. Treitschke and Tammann⁵ record the result of their study of the freezing-point curves of mixtures of iron and sulphur; the microphotographical examination of such mixtures shows that the injurious effects of sulphur on iron arise, in mixtures containing above 2 per cent. of sulphur, from the presence of the fusible sulphide layered between the particles of iron; the brittleness produced by 0.02 per cent. of sulphur is dependent on the properties of the mixed crystals, rich in iron. Vigouroux⁶ has prepared silicides of iron, cobalt, and nickel by the action at high temperatures of silicon tetrachloride on these metals. The compounds so obtained have the formulæ Fe_2Si , Co_2Si , Ni_4Si , and Ni_2Si ; iron silicide is magnetic, the

¹ *Compt. rend.*, 1906, **142**, 274.

² *Ibid.*, 425.

³ *Ibid.*, 189.

⁴ *Trans.*, 1906, **89**, 720.

⁵ *Zeit. anorg. Chem.*, 1906, **49**, 320.

⁶ *Compt. rend.*, 1905, **141**, 828; 1906, **142**, 635 and 1270.

others are non-magnetic. The interaction of iron and silicon, and of nickel and silicon, has also been investigated by means of the freezing-point curves of fused mixtures of these elements. Guertler and Tamman¹ conclude from these results that iron and silicon form compounds of the formulæ FeSi and Fe_2Si , and that nickel and silicon form five compounds, namely, Ni_3Si , Ni_2Si , Ni_3Si_2 , NiSi , and Ni_2Si_3 . A ferric hydrogen sulphate, $\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, is produced as a white crystalline solid by evaporating a solution of ferric sulphate in sulphuric acid.² Rubidium and cæsium iron-selenium alums are formed by dissolving ferric hydroxide in selenic acid and treating the solution with rubidium or cæsium carbonate. The formula of the rubidium salt is $\text{Rb}_2\text{Fe}_2(\text{SeO}_4)_4 \cdot 24\text{H}_2\text{O}$; they both form violet crystals belonging to the regular system.³ Crystals of ferric hydroxide, $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and of the oxide Fe_2O_3 , are formed by acting on crystalline ferric sulphate with caustic soda; the crystals are pseudomorphous with ferric sulphate.⁴

Several researches are recorded dealing with the commercial alloys of iron; Hiorns⁵ has investigated the influence of varying quantities of silicon, phosphorus, manganese, or sulphur on the formation of crystals of cementite, ferrite, or graphite in cast iron. Fettweis⁶ finds, experimenting with iron phosphide, that increase in the proportion of phosphorus diminishes the proportion of carbon dissolved by iron. Roozeboom's theory⁷ is shown by Wüst⁸ not to apply to iron-carbon alloys containing a large proportion of carbon. When the freezing point of iron has been depressed to 1130° by the addition of carbon, further increase in the proportion of carbon has no effect, and graphite does not separate out from the liquid solution. Microscopic examination of the alloys shows cementite to be formed first on solidification; it is not stable below 1000° , is metastable below 700° , and does not break up on prolonged heating. The final condition is ferrite and graphite. The influence of foreign elements on the separation of graphite from cast iron has been studied by adding a weighed amount of the element to a molten cast iron of known carbon content, and determining the proportion of graphite to total carbon in the alloy so produced. Thus tin is found to reduce the solubility of carbon and increase the separation of graphite; iron can, in presence of an excess of carbon, dissolve 16 per cent. of tin. sulphur reduces the solubility of carbon in iron, but does not promote its conversion

¹ *Zeit. anorg. Chem.*, 1905, **47**, 163, and 1906, **49**, 93.

² Komar, *Chem. Zeit.*, 1906, **30**, 15.

³ Roncagliolo, *Gazzetta*, 1905, **35**, ii, 553.

⁵ *J. Chem. Soc. Ind.*, 1906, **25**, 50.

⁷ *Zeit. physikal. Chem.*, 1900, **34**, 437.

⁴ *Ber.*, 1906, **39**, 2270.

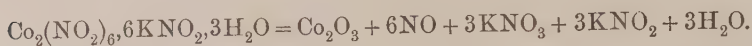
⁶ *Metallurgie*, 1906, **3**, 60.

⁸ *Metallurgie*, 1906, **3**, 1.

into graphite; in fact, it neutralises the influence of silicon promoting the separation of graphite. In a silicon-free iron, phosphorus in amounts below 2.5 per cent. has no effect on the carbon, but above this amount it causes the separation of graphite. In the presence of 0.9 per cent. of silicon the separation of graphite is produced by 3 per cent. of phosphorus (Wüst).¹ The reduction of mixtures of ferric oxide and tungsten dioxide with aluminium yields homogeneous alloys, from which by treatment with hydrochloric acid the ferrotungsten Fe_3W_2 can be obtained (Vigouroux).² Steels of low-carbon content can be alloyed with copper, forming homogeneous alloys which contain a maximum of 32 per cent. of copper, whereas with steels of high-carbon content alloys containing a maximum of 16 per cent. are formed. The physical and mechanical properties of a series of these copper steels have been examined by Breuil.³

Nickel and antimony alloy readily, and appear to form four compounds, of the following compositions, NiSb , Ni_3Sb_2 , Ni_4Sb_5 , and Ni_4Sb . The first is the colour of copper, and is hard and brittle; Ni_3Sb_2 is grey, and although harder than the former is not so brittle. Some of these alloys are magnetic (Lossew).⁴

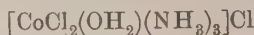
The composition of Fischer's salt (potassium cobaltinitrite) is shown by Rây⁵ to be $\text{K}_6\text{Co}_2(\text{NO}_2)_{12} \cdot 3\text{H}_2\text{O}$, and its decomposition by heat to be represented by the following equation:



Continuing his investigations of double chromates, mentioned in last year's *Report*, Gröger⁶ has succeeded in preparing from potassium chromate and cobalt chloride a potassium cobaltous chromate,



which crystallises in dark brown needles, and is hydrolysed by water, forming potassium chromate and a basic cobalt chromate. The corresponding sodium and ammonium compounds could not, by reason of their ready hydrolysis, be obtained. The investigation of the salts of cobaltammine is still continued by Werner, who with Bindschedler⁷ shows that trichlorotriamminecobalt, $\text{CoCl}_3(\text{NH}_3)_3$, is the first, and triaquotriamminecobalt chloride, $[\text{Co}(\text{OH}_2)_3(\text{NH}_3)_3]\text{Cl}_3$, is the last of a series, of which the intermediate members have the composition



and $[\text{CoCl}(\text{OH}_2)_2(\text{NH}_3)_3]\text{Cl}_2$, and are formed by the action of caustic soda on dichloroaquatriamminecobalt chloride. By the action of

¹ *Metallurgie*, 1906, **3**, 169.

³ *Ibid.*, 1421; **143**, 346 and 377.

⁵ *Trans.*, 1906, **89**, 551.

⁷ *Ber.*, 1906, **39**, 2673.

² *Compt. rend.*, 1906, **142**, 1197.

⁴ *Zeit. anorg. Chem.*, 1906, **49**, 58.

⁶ *Zeit. anorg. Chem.*, 1906, **49**, 195.

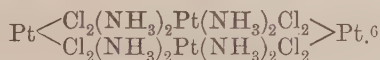
acetic acid and hydrochloric acid on trinitratotriamminecobalt,¹ the triaquotriamminecobalt chloride $[\text{Co}(\text{OH}_2)_3(\text{NH}_3)_3]\text{Cl}_3$ is formed.

The blackish-brown solution produced by the action of carbon monoxide on dilute aqueous solutions of palladous chloride (from 0.005 to 0.05 per cent. of palladium) contains colloidal palladium (Donau).²

An alloy of platinum and iridium containing 10 per cent. of iridium is dissolved slowly by hot concentrated sulphuric acid; the solution boiled with ammonium sulphate gives a precipitate of spongy platinum, the filtrate from which has yielded a number of iridium compounds.³

The observations of Quennessen⁴ show that oxygen takes part in the dissolution of platinum by sulphuric acid, as there is little or no action when these are heated together in a vacuum. A double sulphate of potassium and iridium of the composition $\text{Ir}(\text{SO}_4\text{K})_3 \cdot \text{H}_2\text{O}$ is obtained in bluish-green crystals by the action of sulphuric acid on potassium iridochloride. The solutions give coloured precipitates with many metallic salt solutions (Delépine).⁵

Magnus's green salt is formed by the addition of potassium platinous chloride to platodiammine chloride, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$; if potassium platinichloride is entirely absent then a red isomeride of the green salt is formed; to this the formula $\text{Pt} \left\langle \begin{smallmatrix} (\text{NH}_3)_2\text{Cl}_2 \\ (\text{NH}_3)_2\text{Cl}_2 \end{smallmatrix} \right\rangle \text{Pt}$ is assigned, whilst the green salt is represented by the formula



Hydrazine and hydroxylamine platinocyanides are formed by the interaction of the sulphates of these bases and barium platinocyanide; they are remarkably fluorescent and exhibit different colours with altered hydration.⁷

Werner and Dinklage⁸ describe potassium nitrilobromo-osmonate $(\text{OsNBr}_4)\text{K} \cdot 2\text{H}_2\text{O}$; it is formed by the action of hydrobromic acid on potassium osmiamate; and is obtained in dark red prisms, the treatment of the mother liquors of which with ammonium bromide gives dark brown prisms of the composition $[\text{OsNBr}_5](\text{NH}_4)_2 \cdot \text{H}_2\text{O}$. Rubidium and caesium hydrogen nitrilobromo-osmonates are also described.

A series of alloys of platinum and silver containing from 10 to 60

¹ Jörgensen, *Ber.*, 1882, **15**, 1900.³

² *Monatsh.*, 1906, **27**, 71.

³ Delépine, *Compt. rend.*, 1906, **142**, 631.

⁴ *Ibid.*, 1841.

⁵ *Ibid.*, 1525.

⁶ Jörgensen and Sørensen, *Zeit. anorg. Chem.*, 1906, **48**, 441.

⁷ Levy and Sisson, *Trans.*, 1906, **89**, 125. ⁸ *Ber.*, 1906, **39**, 499.

per cent. of the former metal has been prepared by Thompson and Miller.¹ The action of nitric acid on these alloys is irregular, and it is evident that nitric acid cannot be employed to effect a separation of gold or iridium from platinum when alloyed with silver.

P. PHILLIPS BEDSON.

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 1115.

ORGANIC CHEMISTRY—ALIPHATIC DIVISION.

ALTHOUGH it cannot be said that, during the past year, any very striking or exceptional discovery has been made in the chemistry of the aliphatic compounds, yet a vast amount of important work has been done in this department, and the results obtained certainly mark a steady advance in nearly every direction.

From the nature of the subject it will be readily understood that a report dealing with experiments which cover so wide an area must necessarily take the form of a series of separate, and often isolated, accounts; any attempt at a continuous method of treatment is, of course, out of the question.

The subjects have been considered as far as possible in the usual order of the various organic families or types, but a strict classification under these heads is, in many instances, undesirable.

Hydrocarbons and Combustion.

A new octane, namely, hexamethylethane, $(\text{CH}_3)_3\text{C}\cdot\text{C}(\text{CH}_3)_3$, has been obtained by Henry¹ as a by-product in the preparation of pinacolyl alcohol by Grignard's reaction, and also from bromopentamethylethane by the action of magnesium methyl bromide (see page 82). It is a crystalline solid which melts at 103°.

Clarke and Shreve² found that, during the reduction of methylisobutylpinacene with hydrogen iodide a small quantity of a hydrocarbon is formed which proves to be a new dodecane, namely, dimethyldiisobutylethane, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2$.

It has been shown by Lebeau³ that hydrocarbons of the aliphatic series may be obtained from their halogen derivatives by means of the metalammoniums; methane, for example, is produced from methyl chloride and sodammonium. Chablay⁴ has extended these observations, and shows that ethylene may similarly be obtained from ethylene dichloride; propylene, *ψ*-butylene, isobutylene, and trimethylene result in the same way from their respective bromides. The dichlorides of methylene, ethylidene, and propylidene, on the other hand, yield the paraffins, methane, ethane, and propane respectively. The

¹ *Compt. rend.*, 1906, **142**, 1075.

² *Amer. Chem. J.*, 1906, **35**, 513.

³ *Compt. rend.*, 1905, **140**, 1042.

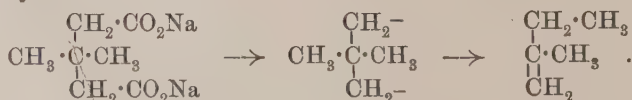
⁴ *Loc. cit.*, 1906, **142**, 93.

same author¹ finds that unsaturated primary alcohols of the aliphatic series react with metalammoniums to give corresponding unsaturated hydrocarbons, propylene, for example, being obtained, in quantitative yield, from allyl alcohol.

A method of preparing olefines is suggested by Mailhe² which consists in decomposing the monohalogen-substituted paraffins by means of reduced nickel, cobalt, or copper. The products, halogen-acid and olefine, are afterwards separated by means of caustic alkali. Dry chlorides of bivalent metals behave similarly as catalytic agents in bringing about this decomposition; chlorides of univalent metals appear to be inactive. From these results the author assumes the formation of intermediate compounds, $C_nH_{2n} \cdot (MCl)Cl$, in the former case.

The simple hexatriene, $CH_2 \cdot CH \cdot CH \cdot CH \cdot CH_2$, was obtained by van Romburgh and Dorssen (1905) by the action of heat on the di-formate of *s*-divinylglycol. Smedley³ has lately carried out a series of investigations with the object of preparing hexatrienes from *aa*-dichloropropylene and its homologues; it is found that when the latter compound is heated with metallic sodium in petroleum at about 80° a small quantity of diallyl is produced, whereas it had been stated by previous observers that these two substances do not interact. There is produced also a small quantity of a liquid which boils at 80° which is probably identical with the hexatriene above mentioned.

It was shown by Walker in 1893 that sodium *o*-ethyl camphorate, on electrolysis, yields the ester of an unsaturated acid, subsequently proved to be an $\alpha\beta$ -compound (*isolauronolic acid*). Camphoric acid being a derivative of glutaric acid, it follows that during electrolysis of the above-named salt a methyl group moves from one carbon atom and becomes attached to an adjacent one. Potassium glutarate also on electrolysis yields, not trimethylene, but propylene, the result indicating that here again the migration of an atom of hydrogen must have occurred.⁴ It became, therefore, a matter of interest to ascertain the behaviour of $\beta\beta$ -dimethylglutaric acid since, in this case, such a transference of the hydrogen atom is impossible, and if an open chain hydrocarbon is produced it must result from the transference of a hydrocarbon group as a whole. Walker and Wood⁵ find that the result in this case is unsymmetrical methyl-ethylethylene:



¹ *Compt. rend.*, 1906, **143**, 123.

² *Chem. Zeit.*, 1906, **30**, 37.

³ *Proc.*, 1906, **22**, 158.

⁴ Vanzetti, *Atti. R. Accad. Lincei*, 1904 [v], **13**, ii, 112.

⁵ *Trans.*, 1906, **89**, 598.

There is therefore a fundamental rearrangement of the carbon nucleus, a four-carbon chain resulting from one of three carbon atoms.

H. Jackson¹ and D. Northall-Laurie have studied the change which takes place when acetylene is subjected to electrical discharges of high frequency. It is found that a semi-solid brown substance is produced which sets to a hard and very insoluble solid on exposure to air. If care is taken to avoid secondary reactions the composition of the product is the same as that of acetylene. This substance, which is apparently a polymeride of acetylene, readily absorbs oxygen up to about 8 per cent. When heated out of contact with air it yields a volatile oil together with a small quantity of methane and hydrogen. The same authors² have also studied the behaviour of methyl alcohol and of acetaldehyde when their vapours are subjected to high-frequency discharges. They find that, with discharges of very short duration, methyl alcohol yields carbon monoxide and hydrogen, whilst acetaldehyde gives methane and carbon monoxide together with some acetylene and water. Both these changes are reversible, the latter more readily than the former. The authors have continued the experiments, which were initiated by one of them some time ago, on a number of saturated and unsaturated compounds, and they conclude that in the case of paraffin derivatives the general tendency is for unsaturated compounds to give polymeric varieties under the influence of the discharges, whilst saturated compounds under similar conditions yield substances of simpler structure.

Experiments on the direct union of carbon and hydrogen have hitherto been carried out either at temperatures of 1100—1300° or at the temperature of the electric arc between carbon electrodes in hydrogen. Pring and Hutton³ have recently made a series of observations on the course of the reaction at temperatures from 1000° up to about 2800°. Their results indicate that the proportion of methane formed is much smaller than was to be expected from the results of some former observers and that the yield is still lower if the carbon rods have been previously purified by heating to a high temperature in chlorine. The formation of acetylene is just perceptible at 1700° and becomes progressively greater with increase of temperature up to about 2500°.

Bone and Drugman⁴ have made extensive experiments on the propagation of a flame, under ordinary conditions, through mixtures of typical hydrocarbons with amounts of oxygen insufficient for complete combustion; from their results they infer that there is no essential difference between the mechanism of combustion above and below the ignition point, both phenomena involving the initial formation of hydroxylated molecules. These conclusions are based chiefly

¹ *Proc.*, 1906, **22**, 155.

² *Loc. cit.*, 156.

³ *Trans.*, 1906, **89**, 1591.

⁴ *Loc. cit.*, 660.

on the fact that there is a remarkable contrast between the behaviour of olefines and paraffins when exploded with a proportion of oxygen represented by the relation $C_xH_y + x/2O_2$, and also on the phenomena associated with the inflammation of a mixture of an olefine with much less oxygen than is represented in this expression. The same authors and Andrew¹ have further investigated the behaviour of mixtures of oxygen with ethane and with ethylene, in the proportions $C_2H_6 + O_2$ and $3C_2H_4 + 2O_2$, in such a manner that some discrimination could be made between the various products of combustion according as they arise at an earlier or later stage in the flame. The results indicate that there is probably no essential difference between "detonation" and "inflammation" so far as the result of the initial encounters between individual molecules of hydrocarbon and oxygen is concerned.

The same authors² have made experiments with the object of ascertaining whether the presence of water vapour has an influence on the combustion of a hydrocarbon which is at all comparable with that exerted in the cases of carbon monoxide and of hydrogen. Ethylene and acetylene were selected for experiment, since it had been previously shown that no steam is produced in the initial stages of their slow combustion. The results were compared when the dried and the undried hydrocarbons were heated, under similar conditions, with oxygen, and the authors conclude that the rigid exclusion of moisture, by means of the best known methods of desiccation, has little if any influence on the rate of oxidation of a hydrocarbon.

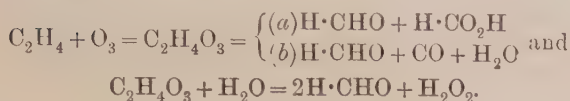
Action of Ozone.

Drugman³ has made a further study on the oxidation of hydrocarbons by ozone at low temperatures, and his results show that there is a radical difference between the behaviour of saturated and unsaturated hydrocarbons. In the case of saturated hydrocarbons, gradual hydroxylation of one carbon atom takes place; the alcohol is first formed and is then quickly oxidised to the relatively stable aldehyde and more slowly to the acid. Unsaturated hydrocarbons give first an ozonide or peroxide, which readily decomposes, yielding products containing a less number of carbon atoms. Ethylene reacts so violently with ozone, even at very low temperatures, that the initial product could not be isolated; in the moist state, the products of the reaction were formaldehyde, formic acid, and hydrogen dioxide. The changes are probably to be represented as follows:

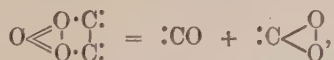
¹ *Trans.*, 1906, **89**, 1614.

² *Loc. cit.*, 652.

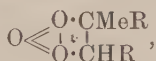
³ *Loc. cit.*, 939.



An extensive series of investigations has been carried out during the last few years by Harries and his colleagues on the behaviour of ozone towards various organic compounds, and a valuable summary of the work has recently been published by the author.¹ In conducting these experiments the substance to be examined is usually dissolved in dry chloroform and a current of ozonised oxygen, mixed with carbon dioxide, is passed into the solution at a low temperature. Under these conditions the danger of explosion is lessened and volatile products are removed in the current of gases. Amongst the many interesting results which have been obtained, the behaviour of unsaturated compounds is perhaps the most important. Unsaturated hydrocarbons or alcohols which contain an ethylene linking combine with one molecule of ozone to give ozonides, which are usually thick oils or syrups and are often explosive. They behave like peroxides in their power of liberating iodine from potassium iodide and in bleaching potassium permanganate or indigo. By the action of water they are decomposed with production of aldehydes, ketones, peroxides of these, or hydrogen dioxide, disruption of the carbon chain occurring at the position of the original double linking. The author represents these ozonides as containing quadrivalent oxygen, although it is perhaps doubtful whether there is here any advantage in making this assumption. On this view the typical decomposition may be represented as



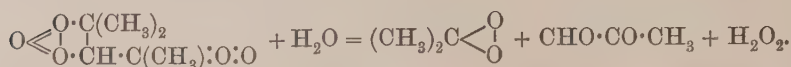
one of the resulting aldehydes or ketones appearing as a peroxide which may yield hydrogen dioxide by action of water. Unsaturated compounds containing a carbonyl group, such as ketones, aldehydes, or monobasic acids, when acted on by ozone in the way above mentioned, are found to combine with four atoms of oxygen instead of three; in the resulting "ozonide-peroxides" the additional atom of oxygen is attached to the carbonyl group. On decomposition by water, the latter oxygen appears as hydrogen dioxide, the ozonide grouping splitting up in the manner above indicated. As examples of these typical decompositions one may refer in the first case to ozonides of the type



which by the action of water give the ketone peroxide and

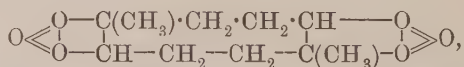
¹ *Annalen*, 1905, **343**, 311.

the aldehyde $R \cdot \text{CHO}$, and secondly to the ozonide of mesityl oxide,¹ which yields acetone peroxide, methylglyoxal, and hydrogen dioxide. The latter decomposition should, in accordance with the author's later view, be represented as follows:



These typical actions of ozonides not only afford simple methods of obtaining various aldehydes, ketones, &c., which have hitherto been unknown or difficult to prepare, but the results may also be applied, in many cases, to the determination of constitution. In the light of the evidence obtained from these researches, the author discusses, for example, the constitution of diallyl, crotonic and isocrotonic acids, oleic and elaidic acids, benzene, naphthalene, and many other compounds.

The behaviour of Para-caoutchouc towards ozone has already been referred to in the last *Report* (p. 80); the diozonide, $\text{C}_{10}\text{H}_{16}\text{O}_6$, which is formed is decomposed by water with production of lævulinaldehyde and its peroxide and lævulic acid. Similar experiments have since been made by Harries² with the hydrocarbon $\text{C}_{10}\text{H}_{16}$ from gutta percha; the results obtained are quite analogous, except that the ozonide gives, on decomposition, a greater proportion of lævulic acid and less aldehyde. The results indicate that the parent hydrocarbons are the same but that the ozonides are different. This difference, the author considers, may be due to stereoisomerism. Representing the hydrocarbon as 1:5-dimethylcyclooctadiene the diozonides will have the constitution



in which the ozonide or methyl groups can be situated in the *cis*- or *trans*-position with respect to the plane of the ring. In order to account for the different behaviour on decomposition, the splitting of one pair of oxygen double linkings in each of the two ozonide groupings may be supposed to occur either in the adjacent or in the opposite pairs.

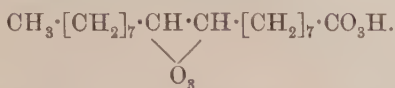
It has already been shown by the author that oleic acid in chloroform solution, when acted on by ozone, combines with four atoms of oxygen, behaving therefore in the normal manner of an unsaturated compound containing the carbonyl group. This product has been further studied by Harries and Thieme.³ When washed with water and sodium hydrogen carbonate it yields the normal ozonide and the aqueous solution

¹ Compare *Ann. Report*, 1905, 74.

² *Ber.*, 1905, **38**, 3985.

³ *Loc. cit.*, 1906, **39**, 2844.

shows strongly marked reactions of hydrogen dioxide. The initial product is therefore oleic acid ozonide peroxide,



The normal ozonide may also be obtained by ozonising oleic acid in acetic acid solution, diluting with water, and neutralising with sodium hydrogen carbonate. Both these products on decomposition with water yield azelaic acid or its semialdehyde and nonylic acid or aldehyde; hydrogen dioxide is produced in both cases, but in much larger proportion from the ozonide peroxide.

Molinari and Soncini¹ obtain the normal ozonide by action of ozone on oleic acid itself, without use of a solvent, and also when an acetic acid solution is employed. Under the conditions of their experiments, therefore, only three atoms of oxygen would appear to be taken up by one molecule of the acid. A question of priority also arises here, since the last-named authors claim to have commenced the study of the action of ozone on various oils in 1903. Weyl, however,² points out that in 1898 he applied for a patent for obtaining disinfecting substances which were prepared by the action of ozone on acids of the oleic series.

A study of the decomposition products of oleic acid ozonide has been made by Molinari and Soncini³ with the object of establishing the constitution of oleic acid. They show that by the action of alkalis four acids are obtained, in addition to a neutral substance which was not identified. These four acids prove to be: (1) azelaic acid, $\text{CH}_2 \cdot ([\text{CH}_2]_3 \cdot \text{CO}_2\text{H})_2$; (2) normal nonylic acid, $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$; (3) a monobasic acid, $\text{C}_{18}\text{H}_{36}\text{O}_3$,

which appears to have the constitution

$$\begin{array}{c} \text{CH}_3 \cdot [\text{CH}_2]_7 \\ \text{CH}_3 \cdot [\text{CH}_2]_7 \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{OH} \\ \text{CO}_2\text{H} \end{array}$$

and (4) a dibasic acid,

$$\begin{array}{c} \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \\ \text{O} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H} \end{array}$$

The formation and decomposition of this normal ozonide leaves no doubt, in the authors' opinion, that the double linking in oleic acid is between the atoms C_9 and C_{10} .

An interesting general method of obtaining the dihalogen derivatives of paraffins is afforded by the reaction discovered by Braun,⁴ which consists in the action of phosphorus pentachloride or pentabromide on cyclic imino-compounds. Benzoylpiperidine, for example, when acted on by phosphorus pentachloride, yields α -dichloropentane and benzonitrile, the latter being easily removed by steam distillation. Braun and Beschke⁵ have recently shown that pyrrolidine behaves similarly.

¹ *Ber.*, 1906, **39**, 2735.

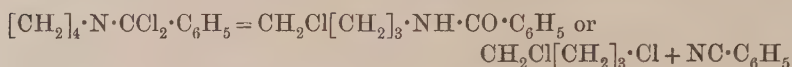
² *Loc. cit.*, 3347.

³ *Loc. cit.*

⁴ *Ann. Report*, 1904, 71.

⁵ *Ber.*, 1906, **39**, 4119.

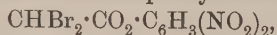
When benzoylpyrrolidine is heated with phosphorus pentachloride, the changes which take place depend somewhat on the conditions, the products being either benzo- δ -chlorobutylamide, or dichlorobutane and benzonitrile: $[\text{CH}_2]_4 \cdot \text{N} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \rightarrow [\text{CH}_2]_4 \cdot \text{N} \cdot \text{CCl}_2 \cdot \text{C}_6\text{H}_5$ and



By the same type of reaction Braun and Schmitz¹ have obtained dichloro- and dibromo- octanes from coniine. Benzoylconiine, when heated with phosphorus pentachloride, gives in the first instance the 'amide-chloride,' $\text{C}_3\text{H}_{16} \cdot \text{N}(\text{Cl}_2)\text{C}_6\text{H}_5$, and this, when quickly distilled, breaks up into dichloro-octane and benzonitrile, as in the previous example.

Nef, in 1897, came to the conclusion that certain halogen-substitution products of the hydrocarbon C_2H_2 must be regarded, not as acetylene compounds, but as derivatives of acetylidene, $\text{H}_2\text{C}:\text{C}$, containing bi-valent carbon. At first it appeared probable that compounds of both types might exist, such as the mono- and di-substituted acetylenes, $\text{RC}:\text{CH}$, $\text{RC}:\text{CR}$, and the isomeric acetylidenes, $\text{RHC}:\text{C}$, $\text{R}_2\text{C}:\text{C}$. But this appears not to be the case, since all the known halogen-substituted hydrocarbons corresponding with these formulæ, such as Behrend's di-iodoacetylene, Sabanéeff's monobromoacetylene, and Wallach's monochloroacetylene, are to be regarded, according to Nef, as acetylidene derivatives. The so-called iodoacetylene of Baeyer is stated to be, in reality, di-iodoacetylidene. The monohalogen-derivatives of alkylated and arylated acetylenes, however, such as $\text{CH}_3 \cdot \text{C}:\text{Cl}$ and $\text{C}_6\text{H}_5 \cdot \text{C}:\text{CX}$, can be isolated; they prove to be sweet-smelling and 'harmless,' whereas the acetylidene compounds are highly poisonous, sometimes spontaneously combustible, and have a disagreeable odour.

Lemoult, in 1903, by the action of alcoholic potash on tribromoethylene, obtained a compound which he regarded as dibromoacetylene, but which is probably also an acetylidene compound. It is now shown by Lawrie² that the latter substance unites with hydrogen iodide to give an addition compound, $\text{C}_2\text{Br}_2 \cdot \text{HI}$, which is obtained as a heavy oil. When this product is oxidised by nitric acid it yields dibromoacetic acid and iodine, and when treated with alcoholic sodium phenoxide it gives unsymmetrical phenyl dibromovinyl ether, $\text{Br}_2\text{C}:\text{CH} \cdot \text{O} \cdot \text{C}_6\text{H}_5$. That the two bromine atoms are here united to the same carbon atom is shown by the fact that nitric acid converts the compound almost quantitatively into isomeric dinitrophenyl dibromoacetates,



and these by the action of ammonia yield the isomeric dinitrophenols and dibromoacetamide.

From these and other observations the author concludes that the

¹ *Ber.*, 1906, **39**, 4365.

² *Amer. Chem. J.*, 1906, **36**, 487.

mono- and di-halogen substituted acetylenes are unknown and that it is extremely improbable that such compounds will be isolated.

Alcohols, Aldehydes, and Ketones.

Henry¹ proposes to distinguish tertiary from primary and secondary alcohols by the actions of acetyl chloride; this reagent converts primary and secondary alcohols quantitatively into acetic esters, whilst tertiary alcohols yield the corresponding chlorides. With fuming hydrochloric acid again, tertiary alcohols, except those of high molecular weight, are at once converted into chlorides even in the cold, whereas primary and secondary alcohols are not esterified unless the mixture is heated. The author is of opinion² that tertiary alcohols are to be regarded as alcohols *par excellence* and that in them the true alcoholic function is most simply represented, since, in their behaviour, they most nearly resemble metallic hydroxides. The latter react with acetyl chloride, for example, to give a metallic chloride and acetic acid, and the difficulty of preparing the sodium derivative of trimethylcarbinol is compared to the inertness of sodium hydroxide to metallic sodium.

According to the French patent (360,180) of Jouas and others, the preparation of ethyl alcohol from acetylene is effected by passing the gas into a mercuric salt, which causes the precipitation of mercury acetylide. On boiling the resulting mixture, acetaldehyde is produced and the mercuric salt regenerated. The aldehyde is afterwards reduced to alcohol by sodium amalgam, or it may be used for the preparation of acetic acid by oxidation.

Klason and Norlin³ prepare pure methyl or ethyl alcohol by acting on a solution of potassium methyl or ethyl sulphate with rather more than the calculated quantity of pure sulphuric acid, concentrating the distillate by fractionation and by means of potash, and finally removing the last traces of water with filings of metallic calcium. The alcohols so prepared are quite odourless, and are not coloured when heated on a water-bath with an equal volume of sulphuric acid.

As examples of some of the recent applications of Grignard's reaction to the preparation of alcohols, the following may be mentioned. Reif,⁴ by acting with magnesium ethyl bromide on crotonaldehyde, obtains the unsaturated alcohol Δ^{β} -hexene- δ -ol,



and, with magnesium propyl bromide, in a similar way, Δ^{β} -heptene- δ -ol, $\text{C}_3\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{C}_3\text{H}_7$.

¹ *Bull. Acad. roy. Belg.*, 1906, 261.

² *Loc. cit.*, 537, and *Compt. rend.*, 1906, **142**, 129.

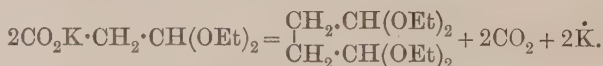
³ *Arkiv. Kem. Min. Geol.*, 1906, **2**, No. 24, 1.

⁴ *Ber.*, 1906, **39**, 1603.

From ethyl chloroacetate and magnesium ethyl bromide Süsskind¹ prepares chloromethyldiethylcarbinol, $\text{CH}_2\text{Cl}\cdot\text{C}(\text{C}_2\text{H}_5)_2\cdot\text{OH}$, and Paal and Weidenkaff,² by the action of magnesium phenyl bromide on ethyl glycollate, obtain diphenylethylene glycol,
 $(\text{C}_6\text{H}_5)_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$.

Fournier³ states that in preparing alkyl bromides by the action of hydrogen bromide on primary or secondary saturated alcohols, it is not necessary, as was supposed, to heat the mixture under pressure. The author prepares a regular current of hydrogen bromide by dropping bromine into toluene in contact with iron wire. The gas is passed into the heated alcohol at a suitably regulated temperature, the excess of hydrogen bromide is afterwards expelled, and the resulting alkyl bromide distilled off. Operating in that way, a yield of 70 per cent. is obtained.

Wohl and Schweitzer⁴ have shown that aliphatic dialdehydes, in the form of their acetals, may be obtained by the electrolytic method, the changes being quite comparable with those which take place in Kolbe's well-known synthesis of hydrocarbons. The double acetal of succinic dialdehyde, for example, results from the electrolysis of potassium β -di-ethoxypropionate :



Potassium diethoxybutyrate similarly yields the double acetal of adipic dialdehyde, acraldehyde acetal being also produced. The dialdehydes themselves are obtained by hydrolysis of the acetals with dilute sulphuric acid. Adipic dialdehyde is in ordinary circumstances very stable, but when heated with water for five hours at 110° with continued agitation, it yields *cyclopentenealdehyde*,



The latter compound was obtained in 1898 by Baeyer and Liebig when attempting the preparation of adipic dialdehyde by the action of lead peroxide on dihydroxysuberic acid.

Haehn⁵ describes a method of preparing ketones by the action of calcium carbide on monobasic fatty acids. The dry acids react in the cold with calcium carbide to produce acetylene; but at a higher temperature the ketones are obtained :



¹ *Ber.*, 1906, **39**, 225.

² *Loc. cit.*, 2062.

³ *Bull. Soc. chim.*, 1906, [iii], **35**, 621.

⁴ *Ber.*, 1906, **39**, 890.

⁵ *Loc. cit.*, 1702.

The water produced then reacts with calcium carbide to produce acetylene and calcium hydroxide or oxide. It might, of course, be thought that the change consists simply in the usual decomposition of the calcium salt, but the author considers that such is not the case, since the products are not necessarily the same. Calcium isovalerate, for example, on heating yields principally valeraldehyde, whereas isovaleric acid and calcium carbide give principally valerone, with only little valeraldehyde.

In a later communication¹ the author suggests that, in the above-mentioned change, the acid anhydride is first produced, and is then catalytically decomposed by fresh calcium carbide into the ketone and carbon dioxide. It is shown, for example, that acetic anhydride when heated with the carbide yields acetone. Ketones are produced in this reaction of acids with calcium carbide at a much lower temperature than by the dry distillation of calcium salts.

With the object of ascertaining whether acetone can behave towards certain reagents as isopropenyl alcohol, $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH}_2$, Taylor² has studied the action of sodium and of magnesium methyl iodide on acetone. It is shown by the author that the so-called sodium-acetone is a mixture of caustic soda with a small proportion of isopropyl oxide; this result indicates that acetone does not contain any hydrogen directly replaceable by sodium under the conditions employed. By the action of Grignard's reagent, at the ordinary temperature and up to 140° , no methane was liberated. In these cases therefore acetone shows no indications of the behaviour above suggested.

The question is discussed by Rothmund³ whether the compounds which acetone forms with alkali sulphites, or bisulphites can exist in aqueous solution. It has been shown that in alkaline photographic development by quinol or pyrogallol, a mixture of acetone and a sulphite may replace the alkali; also if a solution of a sulphite, made neutral towards phenolphthalein by addition of an acid, is mixed with acetone, it becomes alkaline towards that indicator. These results indicate that the change should be represented as $(\text{CH}_3)_2\text{CO} + \text{SO}_3 + \text{H}_2\text{O} = \text{C}_3\text{H}_6\text{O} \cdot \text{HSO}_3 + \text{OH}$, sulphurous acid being approximately dibasic towards phenolphthalein, acetone-sulphurous acid monobasic and the latter being a stronger acid. Electric conductivity and cryoscopic measurements favour this view.

It has been shown by Couturier and Meunier (1905) that acetone reacts with magnesium amalgam to give a compound which probably has the constitution $\text{Mg} \begin{smallmatrix} \text{O} \cdot \text{C}(\text{CH}_3)_2 \\ | \\ \text{O} \cdot \text{C}(\text{CH}_3)_2 \end{smallmatrix}$, and that this is decomposed by

¹ *Arch. Pharm.*, 1906, **244**, 234.

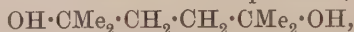
² *Proc.*, 1906, **22**, 173.

³ *Monatsh.*, 1905, **26**, 1545.

water with formation of pinacone hydrate. As a method of preparing pinacone, Holleman¹ modifies this process by acting with magnesium wire on a solution of mercuric chloride in acetone; the yield is about 35 per cent. of the acetone employed.

Henry² finds that pinacolin reacts with magnesium methyl bromide and yields pentamethylethanol, $\text{CMe}_3 \cdot \text{CMe}_2 \cdot \text{OH}$, which Butleroff originally obtained in 1875 by the action of zinc methide on trimethyl-acetyl chloride. This reaction, and the formation of β -cyano- γ -dimethylbutan- β -ol, $\text{CMe}_3 \cdot \text{CMe}(\text{OH}) \cdot \text{CN}$, by the action of hydrogen cyanide on pinacolin, are brought forward as further proofs of the ketonic nature of pinacolin.

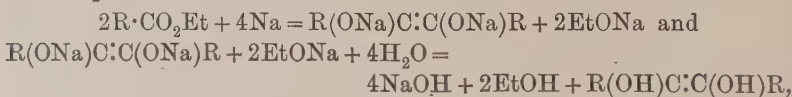
The same author³ shows that succinic pinacone,



is produced by the action of magnesium methyl bromide on ethyl lævulate, $\text{COMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$. Zelinsky in 1902 obtained a compound, which is doubtless identical with this, by action of magnesium methyl bromide on acetonylacetone, $\text{COMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$; the melting points given by these two authors differ, however, considerably. The behaviour of succinic pinacone as a tertiary alcohol is illustrated by its behaviour towards fuming hydrochloric acid or acetyl chloride; these reagents convert it into the corresponding dichlorodimethylhexane, $\text{CMe}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2\text{Cl}$.

Bouveault and Locquin⁴ have published a summary of their interesting work on the action of sodium on esters of the aliphatic series and several new results have also been added. It was shown by Bouveault and Blanc in 1903 that esters may be reduced to the alcohol corresponding to the acid from which the ester is derived by action of sodium in alcoholic solution. Amyl acetate, for example, yields ethyl alcohol, methyl butyrate, *n*-butyl alcohol, and methyl octoate gives *n*-octyl alcohol. The action may even be applied to esters of unsaturated acids, oleyl alcohol, for instance, being obtained from ethyl oleate.

When the dry ester is added slowly to metallic sodium in dry ether, the sodium becomes, after a time, converted into a yellow powder; and this product when decomposed by water yields a ketone-alcohol of the type $\text{R} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{R}$; for these compounds the authors suggest the general name "acyloins." The changes are considered by the authors to take place as follows:



¹ *Rec. trav. chim.*, 1906, **143**, 20.

² *Compt. rend.*, 1906, **143**, 20.

³ *Loc. cit.*, 496.

⁴ *Bull. Soc. chim.*, 1906, [iii], **35**, 629, 636, 637, 641, 643, 646.

the latter compound then immediately undergoing tautomeric change to $R \cdot CO \cdot CH(OH) \cdot R$. A large number of these acyloins have been prepared and examined by the authors; the formation of the first member—methylacetol—has been proved to take place in this general reaction, but the method is not suited for its preparation, owing to the solubility in water and instability of the substance. When the acyloins are reduced, by means of sodium and alcohol, the product consists of a mixture of two stereoisomeric modifications of a symmetric disecundary glycol, $R(OH)CH \cdot CH(OH)R$, and a secondary alcohol, $CH_2R \cdot CRH(OH)$. These products are readily converted into ketones, $R \cdot CO \cdot CH_2R$, by heating with dilute sulphuric acid and by oxidation respectively, so that a general method is afforded of converting acyloins almost quantitatively into ketones of this type.

On oxidation the acyloins yield α -diketones; the usual oxidising agents are not, however, suitable for this purpose, but the authors find¹ that the catalytic method of Sabatier and Senderens² gives good results.

Diphenylketene, $(C_6H_5)_2C:CO$, was obtained by Staudinger in 1905 by the action of zinc on diphenylchloroacetyl chloride. The same author and Klever³ have now prepared the corresponding dimethyl derivative, $(CH_3)_2C:CO$, by acting with zinc on bromoisobutyryl bromide in ether or ethyl acetate solution. The pure substance is a mobile liquid, which is stable at -20° , but readily polymerises at the ordinary temperature, giving a white substance which appears to be the diketone, $[(CH_3)_2C:CO]_2$. With water it gives isobutyric acid, and with aniline and phenylhydrazine it produces the anilide and phenylhydrazide respectively of isobutyric acid. Oxygen converts it into a white explosive powder, which is perhaps a peroxide.

Synthesis and Condensation of Formaldehyde.

The much-disputed question as to the reduction of carbonic acid, directly or indirectly, to formaldehyde is still receiving much attention.

With the object of throwing further light on this question and on the nature of carbon dioxide assimilation, W. Löb⁴ has made an extensive study of the behaviour of various gaseous mixtures when these are submitted to the influence of the silent discharge.⁵

Amongst the many interesting results which were obtained, the following may be mentioned.

¹ *Bull. Soc. chim.*, 1906, [iii], **35**, 650.

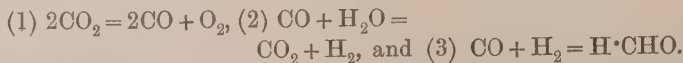
² *Ann. Report*, 1905, **70**.

³ *Ber.*, 1906, **39**, 968.

⁴ *Zeit. Elektrochem.*, 1905, **11**, 745, and 1906, **12**, 282.

⁵ Compare Collie, *Ann. Report*, 1905, **71**.

It is shown that a mixture of carbon dioxide and water-vapour can, under the influence of the silent discharge, yield formaldehyde, the changes probably being :



The author regards this as the first experimental proof which has been given of the production of formaldehyde as a direct reaction product of carbon dioxide. The yield of formaldehyde is increased if the oxygen is removed from the sphere of action by means of reducing substances such as salicylaldehyde, pyrogallol, or chlorophyll. Much larger quantities of formaldehyde were obtained when a mixture of moist carbon monoxide and hydrogen was employed, and in this case the author was able to make the important additional observation that glycollaldehyde is formed as well. It is possible that the glycollaldehyde results from the condensation of formaldehyde.¹ But on the whole it appears more probable that the initial product is an unstable reactive compound, H_2CO , which may perhaps be a tautomeric labile form of formaldehyde, such as $\text{H}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{OH}$.

It is further shown that methane results, in small quantity, when a mixture of carbon monoxide and excess of hydrogen is similarly treated. Losanitsch and Jovitschitsch² have already observed that, under similar conditions, a mixture of methane and carbon monoxide gives rise to acetaldehyde, and although the direct hydrogenisation of acetaldehyde to ethyl alcohol, under the influence of the silent discharge, has not yet been accomplished, the change may fairly be assumed as a step in the natural assimilation process. Finally, it is shown that a mixture of ethyl alcohol, water, and carbon dioxide, when subjected to the action of the discharge, gives, after evaporation, a sugar which, from the character of its osazone, appears to be β -acrose. The latter arises, doubtless, from the condensation of glycollaldehyde. It will be observed that the final change here represents the converse of that in alcoholic fermentation,



Glycollaldehyde is obtained when carbon monoxide is substituted for the dioxide, and also from a mixture of acetaldehyde and carbon monoxide. From a general consideration of the results obtained, the author is of opinion that the natural synthesis of sugars from carbon dioxide may arise in two different directions. The initial unstable product above referred to results from the change $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO} + \text{O}_2$. This product may on the one hand undergo polymerisa-

¹ Compare Pechmann, *Ber.*, 1897, **30**, 2459.

² *Loc. cit.*, 135.

tion into glycollaldehyde and higher sugars; if the velocity of condensation is great as compared with the tautomeric change to formaldehyde, the latter may not actually be formed at all. On the other hand, the initial product may break up in various directions, giving rise to carbon monoxide, hydrogen, methane, &c., and from these acetaldehyde and ethyl alcohol, and finally sugars, may result in the manner above indicated.

For the qualitative recognition of formaldehyde in the experiments here described the author employs the reaction of Pilhashy, which depends on the yellowish-green colour which is given on addition of a few drops of phenylhydrazine, a drop of concentrated sulphuric acid, and heating. Glycollaldehyde was identified by its phenylosazone, oxidation to glycollic acid, condensation to tetrose and hexose, and also by the nitrophenylosazone.¹

Russ² shows that carbon monoxide and hydrogen are produced when formaldehyde vapour is subjected to the action of the silent discharge at 150°.

Bach, it will be remembered, in 1893 stated that by passing a stream of carbon dioxide through solutions of uranyl acetate which were exposed to direct sunlight he obtained a violet precipitate which when exposed became yellow, and was transformed into a mixture of uranous and uranic hydroxides, together with a trace of a brownish substance which he considered to be uranium peroxide. He proposed to explain this result by assuming that formaldehyde and percarbonic acid are first formed, and that the uranium percarbonate which results then undergoes decomposition into uranium peroxide and carbon dioxide. In a later experiment he substituted a salt of dimethylaniline for the uranium acetate, and considered that the production of formaldehyde was confirmed by the formation of tetramethyldiaminophenylmethane (Trillat's test). Euler in 1904 repeated these experiments, and stated that a similar precipitate is obtained from the uranyl acetate solution when a current of hydrogen or nitrogen is substituted for carbon dioxide, and also that in the experiment with dimethylaniline no reaction is obtained if the reagent is carefully purified. The current of gas, in the experiments with uranium, appears only to be instrumental in removing oxygen. Bach³ has since confirmed this view.

Usher and Priestley⁴ state that they have confirmed Bach's (earlier) results, but that the decomposition is extremely small even after three weeks' exposure. They also made similar experiments with liquefied carbon dioxide and uranium acetate solution in sealed tubes. In this case they obtained formic acid and a violet precipitate apparently con-

¹ Wohl and Neuberg, *Ber.*, 1900, **33**, 3107.

² *Zeit. Elektrochem.*, 1906, **12**, 412.

³ *Ber.*, 1906, **39**, 1672.

⁴ *Proc. Roy. Soc.*, 1906, **77**, 369, and **78**, 318.

taining uranium peroxide, but no formaldehyde. Since there are obvious objections to using an organic substance as sensitiser, they repeated the experiments, substituting uranyl sulphate for the acetate. The results obtained in this case were similar; no formaldehyde was detected, but after evaporation of the solution and separation of the formic acid a brown syrup was obtained, which had a bitter taste and reduced Fehling's solution. A similar product was obtained by allowing a solution of formaldehyde to stand for some time in presence of uranic hydroxide. The authors consider that this product resembles Butleroff's methylenitan; it does not, however, react with phenylhydrazine.¹

From these results, and from other observations, the authors conclude that formaldehyde is produced as a transitory intermediate product.² The action of chlorophyll as sensitiser was also investigated: glass plates which had been coated with gelatine and painted with a solution of chlorophyll in light petroleum, or other solvent, were placed in a bell-jar containing moist carbon dioxide, and exposed to light. The chlorophyll became bleached, and the gelatin afterwards gave a pink colour with Schiff's reagent. An aqueous solution of this exposed gelatin gave, on distillation, indications of formaldehyde by the tests mentioned below. The remaining observations deal principally with the problem of carbon assimilation in green plants, and will be considered elsewhere. With reference to the disputed question as to the actual detection of free formaldehyde in the living plant, the authors consider that it is useless to look for the aldehyde in healthy assimilating leaves, since it there undergoes immediate condensation under the influence of protoplasm. But after killing the protoplasm, and destroying enzymes, by immersion in boiling water, leaves which were exposed to sunlight in water saturated with carbon dioxide gave, when subjected to steam distillation, a solution containing formaldehyde. For the identification of formaldehyde in these experiments the authors rely principally on the methylene-aniline test, and also on the formation of hexamethylenetetramine, which they identify by treatment with bromine,³ but details of this are not given.

In connexion with the foregoing statements it would be well to refer to the criticisms of Euler³ on the very similar experiments of Polacci, who in 1899 stated that he obtained a distillate containing formaldehyde from leaves which had been exposed to sunlight and extracted with water.

H. and A. Euler have continued their studies on the behaviour of formaldehyde towards various bases.⁴ As previously stated,⁵

¹ Compare Loew, *J. pr. Chem.*, 1888, **37**, 205; and Fischer, *Ber.*, 1888, **21**, 991.

² Legler, *Ber.*, 1885, **18**, 3343, and Horton, *ibid.*, 1888, **21**, 1999.

³ *Ber.*, 1904, **37**, 3412.

⁴ *Loc. cit.*, 1906, **39**, 36 and 39.

⁵ *Ann. Report*, 1905, 74.

the action takes place in two directions, the condensation to sugars and the production of formates and methyl alcohol. It was shown that the power of different bases in bringing about the condensation does not stand in any simple relation to the rate at which formates are produced. Sugar condensation does not appear to begin until a part of the aldehyde has been changed to formate and methyl alcohol; on the other hand, the concentration at which sugar formation commences is not influenced by the amount of formate present. Reasons are given for considering that the production of formate is preceded by the formation of a metallic "salt" of formaldehyde, or "formolate" as the authors term it. From cryoscopic determinations with mixtures of soda and formaldehyde it is calculated that the dissociation constant of formaldehyde, behaving as an acid, is 1.4×10^{-14} .

In making estimates of the nature and quantity of the sugars produced by condensation it is evident, as the authors point out, that strong alkalis are objectionable as condensing agents, since they tend to destroy or modify the products in question. Advantage is therefore taken of the observation that the condensation of formaldehyde may be brought about by means of calcium carbonate; although the action of this reagent is slow, it has the advantage that the change is effected in practically a neutral solution, and the formate production appears to take place to a less extent.

By heating a litre of 2 per cent. formaldehyde with 10 grams of calcium carbonate for several hours, precipitating the calcium salts with alcohol and ether and distilling the remaining solution, a syrup was left from which, by the action of phenylhydrazine acetate, a yield of osazone was obtained corresponding to 50—80 per cent. of the formaldehyde employed. The crude mixture of osazones so obtained yielded, after purification with benzene, a definite yellow crystalline product which melted at 166° and had the composition of a *pentosazone*. The existence of a pentose in the crude condensation product from formaldehyde was indicated in one of the analyses given by Fischer in 1888. Neuberg also, in 1902, obtained a phenyl methyl osazone from crude formose which melted at 137° and corresponded in composition to a *pentosazone*; this was considered by the author to be derived from a keto-pentose. The pentose obtained in the present case might be either arabinose or ribose; the latter appears, however, to be excluded by the fact that on reduction of the original syrup with sodium amalgam no adonite could be obtained. By oxidation of the syrup with bromine, or nitric acid, a considerable quantity of trihydroxybutyric acid was produced; from these results, and from the behaviour of the syrup with resorcinol and with phenylmethylhydrazine, the authors conclude that the principal condensation product of formaldehyde, under the above-mentioned con-

ditions, is *i*-arabinoketose. From the part of the crude osazone which is more soluble in benzene a *hexosazone* melting at 140—142° was obtained.

If the condensation is interrupted when about half the formaldehyde has disappeared, and the unaltered formaldehyde is then removed by means of *p*-dihydrazinodiphenyl,¹ the remaining solution gives, with phenylhydrazine acetate, a resinous oil from which, by treatment with a mixture of pyridine and light petroleum, a crystalline osazone melting at 180° was obtained. This product corresponds in composition and properties to the osazone of glycollaldehyde. In the process of purifying this osazone by means of pyridine and light petroleum, a substance was deposited from the solution, after some weeks, in the form of colourless scales melting at about 162°; the composition of this product corresponds with that of the hitherto unknown glycollaldehyde hydrazone.

In addition to the above-named substances, the presence of dihydroxyacetone was indicated by means of phenylmethylhydrazine; glyceraldehyde appeared to be absent.

In reference to the experiments which are here described, Loew² points out that in 1888 he succeeded in bringing about the condensation of formaldehyde by means of metallic tin containing some lead, so that the change here occurred in a wholly neutral solution. He considers that the result obtained by Euler with calcium carbonate was due to the initial production of some calcium formate, since he has already shown that the acetates of calcium, lead, or magnesium can act, although slowly, as condensing agents in this way.

That formaldehyde may arise as a degradation-product of sugar is confirmed by the recent experiments of Trillat.³ When sucrose is heated to 100°, or higher temperatures, formaldehyde is produced, the quantities obtained varying from 0·2 to 5·7 per cent. The larger amounts are obtained if the sugar is heated in contact with copper foil. The presence of air is not necessary, although the yield is smaller when air is excluded. Benzaldehyde, acetone, methyl alcohol, acetic acid, acetaldehyde, and phenol derivatives are also produced. Formaldehyde is found not only in the evolved gases, but also in the residual caramel, a fact which perhaps accounts for the antiseptic properties of caramel. It would appear that a portion of the formaldehyde polymerises and forms products analogous to methylenitan, and caramel itself may perhaps be the result of such changes. The caramel-like properties of the products obtained by heating formaldehyde with alkalis are well known.

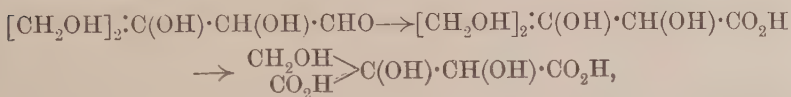
¹ Neuberg, *Ber.*, 1899, **32**, 1961.

² *Loc. cit.*, 1906, **39**, 1592.

³ *Zeit. Ver. Rübenzuck-Ind.*, 1906, 95; and *Compt. rend.*, 1906, **142**, 454.

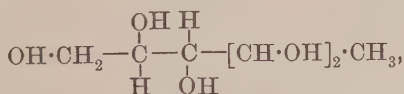
Carbohydrates.

Apiose is the name given by Vongerichten (1900) to a new pentose which is contained, as a disaccharide with α -glucose, in the glucoside apiin found in parsley seeds. The same author and Müller¹ now show that the sugar exists also in the green parts of parsley as well as in the seeds. This pentose, when oxidised with bromine or nitric acid, yields the monobasic apionic acid, and, when further oxidised with nitric acid a dibasic acid is produced which is isomeric with trihydroxyglutaric acid; the relationships of the latter indicate that it is hydroxymethyl-tartaric acid:



With phenylbenzylhydrazine apiose yields a colourless crystalline hydrazone, from which the sugar may be recovered unchanged by means of formaldehyde.

Rhodeose is a methylpentose discovered by Votoček in 1900, and is obtained by hydrolysing convolvulin with dilute sulphuric acid; the glucose which is also present can be removed by fermentation, since rhodeose is non-fermentable. This sugar has been further studied by Votoček and Bulir.² It is shown that on reduction by means of sodium amalgam it yields a corresponding polyhydric alcohol—rhodeitol—which was obtained in white crystalline plates. This substance is not oxidised by the sorbose bacterium, and it therefore follows that its configuration must be represented by the formula



or its image.³ A similar configuration must apply to rhodeose. When rhodeose and its optical antipode fucose are mixed in equal proportions and reduced by sodium amalgam the racemic form of the polyhydric alcohol (*r*-rhodeitol or *r*-fucitol) is obtained.

The trisaccharide melezitose, or melezitriose, has hitherto been regarded as containing three dextrose residues, yielding, it was thought, three molecules of this sugar on hydrolysis. Tanret⁴ now shows that when heated with 20 per cent. acetic acid melezitose yields a mixture of dextrose and turanose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. The latter can be obtained, after removal of the dextrose by fermentation, in the form of hygroscopic, non-crystalline granules containing alcohol, which may be purified by

¹ *Ber.*, 1906, **39**, 235.² *Zeit. Zuckerind. Böhm.*, 1906, **30**, 333.³ Compare Bertrand, *Ann. Report*, 1904, 64.⁴ *Compt. rend.*, 1906, **142**, 1424.

heating to 100°. Turanose is readily hydrolysed by mineral acids, and yields a mixture of equal parts of dextrose and lævulose.

According to Ofner,¹ phenylethylhydrazine reacts with glucose in neutral solution to give the hydrazone, but in acetic acid solution it yields the corresponding osazone; the change takes place more readily than with phenylmethylhydrazine, and the yield is about 60 per cent. Fructose gives about the same yield. This behaviour of glucose affords a further proof that unsymmetrical secondary hydrazines are able to give rise to osazones with aldoses as well as with ketoses.²

Maquenne found that reducing sugars, when treated in a uniform way with phenylhydrazine, showed considerable differences, both in the yield of osazone and in the time required for precipitation; upon these differences Mulliken has since based a scheme for the identification of certain pure sugars. Sherman and Williams³ have now made further experiments in this direction, especially with regard to the influence of dilution and of the presence of other sugars. In the case of glucose and fructose the time required for precipitation varies with the concentration, and is nearly constant for a given dilution, but with fructose the time is about one-third of that required with glucose. From invert sugar the osazone is precipitated almost as quickly as from fructose. In solutions containing about 0.1 per cent. of glucose the precipitation is considerably accelerated by the presence of 1 per cent., or more, of sucrose, but only slightly by 5 per cent. of raffinose. The presence of maltose or of lactose exerts a retarding influence on the precipitation of glucosazone.

It would appear that no direct method has hitherto been devised for the addition of hydrocarbon residues to the carbon chain in pentoses or hexoses, and with this object in view Paal and Hörnstein⁴ have studied the behaviour of Grignard's reagent towards derivatives of glucose such as the penta-acetate and the bromoacetyl derivatives. The latter compounds, however, show but little tendency to react, probably because the aldehydic oxygen of the original glucose is now "ether-linked." But it appeared that the desired result might be attained by employing the lactones of the corresponding monobasic acids produced by oxidation of the aldose sugars; Houben (1904) has, in fact, already shown that tertiary alcohols are obtained by action of Grignard's reagent on lactones. The lactone of *d*-gluconic acid is not itself suitable for this purpose, since it is not soluble in ether or other solvent appropriate to Grignard's reaction, but by acting on *d*-gluconic acid with acetic anhydride a product is obtained which dissolves easily in a mixture of ether and benzene. This product, probably a tetra-aceto-lactone, was not isolated in a pure condition, but was acted on by

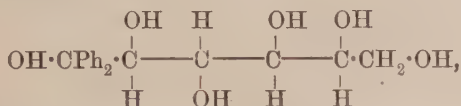
¹ *Monatsh.*, 1906, **27**, 75.

³ *J. Amer. Chem. Soc.*, 1906, **28**, 630.

² Compare *Ann. Report*, 1904, 65.

⁴ *Ber.*, 1906, **39**, 1361.

magnesium phenyl bromide in excess. After decomposition of the resulting products with dilute sulphuric acid the authors obtained, in addition to diphenylmethylecarbinol, a substance which crystallised in white needles; this product is shown to be a hexahydroxydiphenylhexane or diphenylhexitol. From the mode of formation it would appear that the configuration of the latter substance is to be represented by the formula,

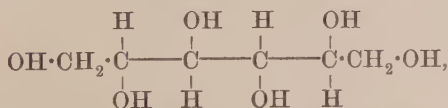


assuming, of course, as is probable, that no steric rearrangement has occurred in the above-mentioned changes. The new compound is therefore to be regarded as 1 : 1-diphenyl-*d*-sorbitol.

In a later communication¹ the authors state that they have isolated the lactone of tetra-acetyl-*d*-gluconic acid as a gummy mass. They have also somewhat modified the details in the preparation of diphenyl-*d*-sorbitol so as to improve the yield.

Paal and Weidenkaff² have since made a similar synthesis from the lactone of tetra-acetyl-galactonic acid, and have obtained in this way another diphenylhexitol. Since the steric configuration of this product is somewhat uncertain, the authors provisionally name it 1 : 1-diphenyl-*d*-galactohexitol.

l-Iditol,



was obtained as a syrup by Fischer and Fay in 1895 from xylose by treatment with hydrocyanic acid and reduction of the resulting *l*-idonic acid or its lactone with sodium amalgam. Bertrand and Lanzenberg³ have now succeeded, by a modification of this method, in obtaining the pure substance in a crystalline state.

A paper of considerable interest has been published by Schade⁴ in which an account is given of a series of investigations on the behaviour of sugar solutions towards alkalis. From the results obtained the author was led to believe that it was possible, in a purely chemical way, and without the use of enzymes, to transform dextrose or lævulose quantitatively into ethyl alcohol and carbon dioxide. It has been previously shown by Framm, in 1896, that the yellow or brown colouring which is usually observed during the action of alkalis on

¹ *Ber.*, 1906, **39**, 2823.

³ *Compt. rend.*, 1906, **143**, 291.

² *Loc. cit.*, 2827.

⁴ *Zeit. physikal. Chem.*, 1906, **57**, 1.

sugar solutions may be prevented altogether if a current of air is passed through the mixture. Schade finds that a similar result may be obtained by operating under reduced pressure or by the addition of hydrogen dioxide. The final products obtained when the first methods are employed appeared to be formic acid and acetaldehyde, the latter being indicated in the distillate. When hydrogen dioxide was added the products were formic acid and acetic acid. The yellow or brown colouring appeared therefore to be due to aldehyde-resin, resulting from the decomposition of acetaldehyde; if the latter was removed, as vapour or by oxidation, the solution remained clear. This view seemed to be supported by the observation that the colouring could also be prevented by the addition of substances which combine with acetaldehyde, such as ammonia, bisulphites, or cyanides. Estimation of the formic acid and acetaldehyde (the latter as acetic acid in the hydrogen dioxide experiment) appeared to indicate that the reaction of alkalis on dextrose or lævulose is to be represented quantitatively by the relation



The question then suggested itself whether it might not be possible to bring about a further reaction between these products in such a manner as to transform them into ethyl alcohol and carbon dioxide. Deville and Debray in 1874 showed that formic acid under the catalytic influence of rhodium-black is resolved into carbon dioxide and hydrogen; the latter then, "in the nascent state," might react with acetaldehyde, converting it into ethyl alcohol. This idea was successfully carried into effect by the author. A 5 per cent. solution of sodium formate, made faintly acid with acetic acid, was warmed to 60° in contact with a small quantity of rhodium-black (colloidal rhodium, prepared by Bredig's method, was found to be ineffective), and the calculated quantity of acetaldehyde, in the form of vapour, was passed gradually into the mixture; in this way a yield of 60—70 per cent. of ethyl alcohol was obtained after three hours. From these results the author concluded that the resolution of sugar into alcohol and carbon dioxide is a spontaneous process which is accelerated by catalysts. Many analogies are pointed out between these purely chemical operations and ordinary fermentation. The final products are reached in the one case by the agency of two different catalysts, namely, hydroxyl ions and rhodium; in the other case by zymase. In both cases the reaction velocity is proportional to the mass of the catalyst or of the enzyme; the changes take place in absence of oxygen and are influenced by the presence of minute traces of foreign substances, by concentration of the solution and by the accumulation of the reaction-products. As in yeast fermentation there appears to be, in the purely chemical process,

an "optimum" temperature which, in the latter case, lies between 40° and 80°.

It is disappointing to learn from a subsequent communication by Buchner, Meisenheimer and Schade¹ that, on repeating certain of Schade's experiments, they have obtained entirely different results, and that the conclusions arrived at by this author can no longer be maintained. The volatile aldehydic substance which was regarded as acet-aldehyde appears to have been furfuraldehyde, and is only produced in small quantity. The yield of formic acid is greater than that above stated, and, in addition, there is formed trihydroxybutyric acid, glycollic acid, and probably a mixture of hexonic acids, &c. The authors consider that formic acid is not a primary product in this decomposition, but that glyceraldehyde is first formed; this under normal conditions would be transformed into methylglyoxal and so into lactic acid; but in the present case it might split up into three molecules of formaldehyde, which would then be oxidised by the hydrogen dioxide as shown by Blank and Finkenbeiner.² The yellow or brown colouring above referred to is caused, the authors consider, by some non-volatile and easily oxidisable hydroxyaldehyde, possibly glyceraldehyde.

Purdie and Young³ find that when methylrhamnoside is completely methylated by means of silver oxide and methyl iodide it yields trimethylrhamnoside, which, on hydrolysis, gives trimethylrhamnose. Dimethylrhamnose is similarly obtained from acetonerhamnoside. Dimethyl- and trimethyl-rhamnose display the ordinary properties of reducing sugars and give crystalline phenylhydrazones.

Trimethyl arabinose is obtained in a similar way from Fischer's α -methylarabinoside.⁴

Irvine and Moody⁵ show that when solutions of the equilibrium mixture of tetramethyl glucose in ordinary organic solvents are cooled from +20° to -20°, the specific rotations undergo very little alteration, and, on again heating to the initial temperature, the original values are exactly obtained. When, however, an alkyl iodide is used as solvent the specific rotation at first slightly increases and then rapidly diminishes, as the solution is cooled. On reheating to 20° distinct downward mutarotation was observed before the initial value was reached. The same regularities were shown by solutions of molecular proportions of the sugar and alkyl halide or hydrogen chloride in carbon tetrachloride. The authors consider that these results point to the formation of oxonium compounds of the sugar with alkyl halides, and the α -form of the aldose appears to be more reactive than the β -isomeride. Tetramethyl α -methylglucoside also behaves abnormally

¹ *Ber.*, 1906, **39**, 4217.

² *Loc. cit.*, 1898, **31**, 2979.

³ *Trans.*, 1906, **89**, 1194.

⁴ Purdie and Rose, *loc. cit.*, 1204.

⁵ *Loc. cit.*, 1578.

when cooled in ethyl iodide solution, but the β -isomeride shows no indication of combining with the solvent.

Amongst other papers which have been published in connexion with the chemistry of sugars, attention should be drawn to the work of Caldwell¹ on the sacroclastic action of acids, in which the author discusses the important question of "weight-normal" versus "volume-normal" solutions; also a paper by Rosanoff,² which contains a criticism of Fischer's *d* and *l* classification of stereoisomerides and suggests a revised nomenclature which will include also the polyhexoses. These papers will be more appropriately referred to in the sections on physical chemistry and stereochemistry.

The highest product of the acetylation of cellulose was at one time considered to be a tetra-acetate, $C_6H_6O(OAc)_4$. The existence of such a derivative would not be in accord with the constitutional formula proposed by A. G. Green, which in other respects gives a very complete indication of the chemical relationships of cellulose.³ This author and A. G. Perkin⁴ have reinvestigated this supposed tetra-acetate, and have determined the acetyl groups by three different methods, and they come to the conclusion that the compound in question is beyond doubt a triacetyl derivative. They admit that higher acetylated products may be obtained if condensing agents such as zinc chloride or sulphuric acid are present, but these, they consider, are derivatives of the hydration products of cellulose and not of cellulose itself. With regard to Green's constitutional formula, it is pointed out that it is only intended to represent cellulose in its simplest or unpolymerised form, in which, for instance, it may be present in an ammoniacal cupric solution. The cellulose of fibres may be regarded either as a physical aggregate of these simple molecules or as a chemical polymeride made up of a number of C_6 complexes, of the structure suggested, united together by means of their oxygen atoms.

Cross and Bevan, as pointed out in the *Annual Report* of last year (page 89), regard the matter from a different standpoint, and their views are expressed at length in their recently published *Researches on Cellulose*, II., 1900—1905.

The cellulose acetates have also been examined by H. Ost.⁵ The soluble acetates were prepared by various different methods, such as those of Cross and Bevan, Lederer and Bayer, and in all cases the same product was obtained, namely, the triacetate, $C_6H_7O_2(OAc)_3$. The author considers, however, that it is questionable whether a triacetate of normal cellulose exists, and that the products obtained are rather to be regarded as acetates of a series of hydrocelluloses of

¹ *Proc. Roy. Soc.*, 1906, **78**, 272.

² *J. Amer. Chem. Soc.*, 1906, **28**, 114.

³ See *Ann. Report*, 1904, 69.

⁴ *Trans.*, 1906, **89**, 811.

⁵ *Zeit. angew. Chem.*, 1906, **19**, 993.

various degrees of degradation. He estimates the acetyl groups in these compounds by hydrolysis with dilute sulphuric acid and distillation of the resulting acetic acid with steam, and considers that the supposed existence of the tetra-acetate is accounted for by the high results obtained when the saponification is effected by alcoholic potash, a process which may give rise to the production of acids at the expense of part of the cellulose.

Glucosides.

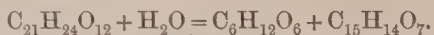
In order to establish the structural formulæ of glucosides, it has been the custom in the majority of cases to rely only upon a study of the products obtained on hydrolysis; in comparatively few instances has the evidence obtained in this way been supplemented by a direct synthetical preparation of the glucoside itself. In order to obtain evidence bearing upon the linking of the sugar residue, Irvine and Rose¹ show that it is necessary to prepare derivatives of the glucoside and to study the hydrolysis of the compounds so obtained. Alkylated glucosides are well adapted for such work owing to the stability of the alkyloxy-groups, the occurrence of secondary changes during hydrolysis being in this way largely precluded. It has previously been shown by Purdie and Irvine (1903) that when the crystalline tetramethyl glucose, prepared from either the α - or β -tetramethyl glucoside, is oxidised, it is converted into tetramethylgluconolactone, this result indicating that the parent glucosides possess the γ -oxidic linking. Similar reactions have now been applied with the object of establishing the complete structural formula of a natural glucoside, salicin being selected as a typical example. Previous investigations have proved salicin to be saligenin β -glucoside, and its synthetical formation from helicin proves that the two parts of the molecule are united through the phenolic hydroxyl group. The authors have now obtained a pentamethyl salicin by the usual method of alkylation with methyl iodide and silver oxide; it is a colourless crystalline compound, practically insoluble in water, but readily soluble in organic solvents. The hydrolysis of this compound presented, however, considerable difficulty, and the following synthetical method was therefore devised in order to prove the γ -oxidic linking. Saligenin and tetramethyl glucose were condensed to saligenin tetramethyl glucoside by heating with hydrochloric acid in benzene. The remaining hydroxyl group was now alkylated by the silver oxide method, and a compound was thus obtained, which proved to be identical in every way with the pentamethyl salicin prepared, as described above, from the natural glucoside.

¹ *Trans.*, 1906, **89**, 814.

Neilson¹ finds that the hydrolysis of salicin and amygdalin can be brought about by the catalytic influence of platinum black. In the case of salicin, the hydrolysis could be conducted under conditions exactly comparable with those of enzyme action, but with amygdalin it was necessary to use open flasks since the hydrocyanic acid produced in the reaction had a strong inhibitive influence on the catalysis. According to Loew and Asö,² platinum black has the power of converting maleic acid into fumaric acid; and Neilson³ states that starch may be hydrolysed by platinum black.

A substance is contained in the cell sap of the leaf epidermis of various plants which gives a blue colour with iodine. The colour disappears on warming, but returns on cooling, as in the case of starch; it is not, however, confined to well-marked grains, but extends uniformly throughout the cell as a fine blue precipitate. The substance which gives this reaction, often called "soluble starch" by botanists, has now been isolated by Barger,⁴ and proves to be a glucoside. It crystallises in microscopic needles, has the composition $C_{21}H_{24}O_{12} \cdot 2H_2O$, and is optically active. The name saponarin is adopted for this new glucoside in reference to the source (*Saponaria officinalis*) from which it was prepared, leaving open the question of its probable identity with the "soluble starch" of other plants.

When hydrolysed with acids it gives rise to glucose and vitexin, a colouring matter which was obtained by A. G. Perkin (1898) from a New Zealand dye-wood.



Another colouring matter is produced at the same time, which appears to be isomeric with, or closely related to, vitexin; for this the author suggests the name saponaretin.

[It may be mentioned here that the much-disputed question as to the nature of the blue substance produced from starch and iodine has been attacked by Padoa and Savarè⁵ in a new way. They investigate the changes in electric conductivity of a solution of iodine in potassium iodide which are caused by addition of given quantities of starch, and they conclude that the blue substance is an additive compound of iodine, starch, and potassium (or hydrogen) iodide, the starch and iodine being present in the ratio $4C_6H_{10}O_5 : I$.]

Further studies of the occurrence of cyanogenetic glycosides have been made by Dunstan, Henry, and Auld,⁶ Guignard,⁷ Hébert,⁸ and Bertrand.⁹

¹ *Amer. J. Physiol.*, 1905, **15**, 148.

² *Bull. Coll. Agr. Tōkyō*, 1906, **1**.

³ *Amer. J. Physiol.*, 1906, **15**, 412.

⁴ *Trans.*, 1906, **89**, 1210.

⁵ *Gazzetta*, 1906, **36**, i, 313.

⁶ *Proc. Roy. Soc.*, 1906, **78**, 145, 152.

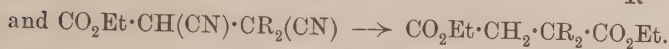
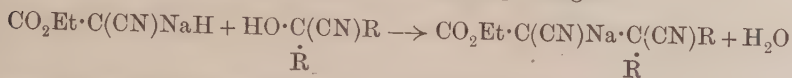
⁷ *Compt. rend.*, 1906, **142**, 545; **143**, 451.

⁸ *Bull. Soc. chim.*, 1906, **35**, 919.

⁹ *Compt. rend.*, 1906, **143**, 832.

Acids.

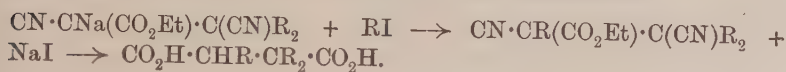
Thorpe and Higson¹ describe a new method of obtaining succinic acid and its alkyl derivatives which is based upon the condensation of ethyl sodiocyanoacetate with the cyanohydrin of either an aldehyde or a ketone, and subsequent hydrolysis of the resulting ethyl ester. The general reaction is indicated by the following changes :



Formaldehydecyanohydrin and ethyl sodiocyanoacetate, for example, yield succinic acid, and benzaldehydecyanohydrin, in a similar way, gives phenylsuccinic acid.

When, however, the condensation of formaldehydecyanohydrin and the cyanoacetate is brought about in hot solution, the product is ethyl *αα'*-dicyanoglutarate, and from this product glutaric acid is obtained on hydrolysis.

The condensation-product $\text{CO}_2\text{Et} \cdot \text{CN} \cdot \text{C}(\text{CN})\text{R}_2$ which is first formed in the above reaction is stable in presence of cold water, so that it is not affected by the small quantity of water produced in the change. If this product is then directly acted on by alkyl iodides, the higher alkyl derivatives of succinic acid can be obtained :



In this way, for example, acetonecyanohydrin, when condensed with ethyl sodiocyanoacetate, gave a product from which, by the action of methyl iodide, trimethylsuccinic acid was prepared.

R. Meyer and Bock² have sought for an improved method of obtaining *isosuccinic* acid, since the directions usually given for the malonic ester synthesis did not yield a pure product, and the preparation from *α*-bromopropionic acid and potassium cyanide was found to be unsatisfactory. An attempt to attain the desired object by means of Grignard's reaction—that is by acting with magnesium on *α*-bromopropionic ester in order to obtain the compound $\text{CH}_3 \cdot \text{CH}(\text{MgBr}) \cdot \text{CO}_2\text{Et}$ and treating this product with carbon dioxide—gave a negative result. Finally, the authors consider that the best method of preparation consists in first obtaining pure *isosuccinamide* (from the impure ester) and hydrolysing this by means of sodium hydroxide. The properties of *isosuccinic* acid and its salts, &c., have been further studied and its heat of combustion re-determined.

¹ *Trans.*, 1906, **89**, 1456.

² *Annalen*, 1906, **347**, 93.

Results of considerable importance have been obtained by Lossen and his colleagues¹ in a series of investigations on the halogen derivatives of aliphatic acids. It will only be possible, in the limited space here available, to give a brief indication of some of these results which are of more general interest.

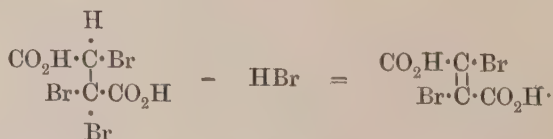
Chloro- and bromo-acetic acids when boiled with bases yield not only glycollic acid but also diglycollic acid, the results depending on the nature and proportion of base. Trichloro- and tribromo-acetic acids when similarly treated give chloroform and carbon dioxide, or, under other conditions, a formate, chloride or bromide, and carbonate.

α -Bromopropionic acid yields both lactic and acrylic acids, whereas β -bromopropionic acid gives hydracrylic and acrylic acids; in the latter case the proportion of acrylic acid is larger and the change takes place more rapidly, contrary to what would be expected from Wislicenus's theory.

$\alpha\alpha$ -Dibromopropionic acid gives pyruvic and α -bromoacrylic acids and the so-called "acryl colloid." The latter, which appears to have the composition $(C_3H_4O_3)_x$, is probably a polymeride of pyruvic acid.

$\alpha\beta$ -Dibromopropionic acid decomposes more rapidly than the $\alpha\alpha$ -acid, and yields glyceric acid with α -bromohydracrylic acid and a small quantity of pyruvic acid; according to theory, the $\alpha\alpha$ -acid should decompose more rapidly.

Tribromosuccinic acid has hitherto been but little studied; it was obtained originally by Petri by the action of bromine on bromomaleic acid. His method of preparation presented, however, certain difficulties, especially as the solution obtained was evaporated at the ordinary temperature, an operation which may take some weeks. The authors have considerably improved this method, and find that the acid may be precipitated by passing hydrogen chloride into the solution. When boiled with caustic potash it yields dibromomaleic acid, and a similar result is obtained when a benzene solution of the acid is heated for two hours, the yield then being almost quantitative. This result again is opposed to theory, since the formation of dibromofumaric acid was to be expected:



Dibromomaleic acid is also produced when dry ammonia acts on tribromosuccinic acid in absolute alcoholic solution; but if aqueous

¹ *Annalen*, 1905, **342**, 112, 157; 1906, **348**, 261.

ammonia is gradually added to an aqueous solution of the acid, the ammonium salt of bromofumaric acid results :



By the action of chlorine water on the normal sodium salt of fumaric or maleic acid, the authors have obtained chloromalic acid, $\text{CO}_2\text{H}\cdot\text{CHCl}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$; it was also obtained by the action of sodium hypochlorite on the acid salt or of hypochlorous acid on the free acids.

Chloromalic acid when subjected to dry distillation, or when heated with concentrated hydrochloric acid, yields chloromaleic acid; on reduction by means of zinc it gives malic acid. When an aqueous solution of the acid is boiled, aldehyde and tartaric acid are produced :



Bromomalic acid was similarly prepared, and its behaviour is in almost every respect analogous to that of the chloro-derivative.

An acid of considerable interest is obtained by the action of alkalis on chloro- or bromo-malic acid; when either of these acids is treated, at the ordinary temperature, with caustic soda, the mixture allowed to stand, acidified and extracted with ether and ethyl acetate, a crystalline product is obtained which melts at 203° and has the composition $\text{C}_4\text{H}_4\text{O}_5$. Analysis of its salts, esters, chlorides, and amide shows the acid to be dibasic. The absence of alcoholic hydroxyl is shown by the fact that both acetyl chloride and phenylcarbimide are without action on the dimethyl ester. The authors therefore assign to this acid the constitution $\text{O} < \begin{array}{c} \text{CH}\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}\cdot\text{CO}_2\text{H} \end{array}$, and name it fumarylglycidic acid. Its formation from chloromalic acid is represented thus :



An aqueous solution of fumarylglycidic acid, when boiled, gives rise to racemic and *i*-tartaric acids, aldehyde and carbon dioxide.

The authors have also studied the decomposition of bromomaleic and bromofumaric acids, and the preparation and reactions of acetylenedicarboxylic acid.

Experiments bearing on the constitution of fulminic acid by Wöhler and Theodorovits were referred to in the previous *Report* (pp. 98—99), from which it appeared that fulminic acid is not formed from mono-carbon compounds by action of nitric acid and mercuric nitrate. These results appeared to speak in favour of the double formula for fulminic acid, but Wöhler's measurements of the molecular weight and equivalent conductivities of sodium fulminate pointed to the single formula HCNO .

Nef, it will be remembered, regards fulminic acid as $C:NOH$ or carbonyl oxime. Jowitschitsch¹ has again attacked this question, and considers that this formula is improbable for several reasons; bearing in mind, for example, the reactivity of nitric acid with unsaturated carbon compounds, one would not expect an unsaturated mono-carbon compound to be produced, almost quantitatively, by the action of nitric acid on a saturated two-carbon compound. The author is inclined rather to prefer the glyoxime peroxide formula, $\begin{matrix} CH:N \cdot O \\ | \\ CH:N \cdot O \end{matrix}$, which was proposed by Scholl,² and has therefore synthetically prepared a compound corresponding to this constitution in order to compare its properties with fulminic acid.

The peroxide of diisonitrososuccinic ester, $\begin{matrix} C(CO_2Et):N \cdot O \\ | \\ C(CO_2Et):N \cdot O \end{matrix}$, was first prepared (from the nitrolic acid of ethyl acetoacetate), and this, by the action of sodium hydroxide under stated conditions, gave rise to the sodium salt of glyoxime peroxide, from which the silver salts were prepared. The di-silver salt closely resembles silver fulminate; it is explosive, and yields hydroxylamine by the action of hydrochloric acid, but differs from silver fulminate in being easily soluble in nitric acid and less explosive. By the action of hydrochloric acid on a nitric acid solution of the silver salt, the free glyoxime peroxide was obtained in small quantity as a yellow, acid liquid.

Esters.

Ethyl nitrocentricarboxylate, $N(CO_2Et)_3$, was prepared by Diels in 1903 by heating a mixture of ethyl chlorocarbonate and ethyl carbamate with sodium. Attempts to saponify this ester with alkalis were not successful, since under these conditions it splits up into ethyl alcohol, carbon dioxide, and ethyl iminodicarboxylate, $NH(CO_2Et)_2$. In this case, therefore, both carbethoxy-groups remain attached to nitrogen. It is now shown by this author and Wolf³ that a different decomposition occurs when the ester is acted on by dry ferric chloride, the products then being ethyl carbonate and ethyl carbimide-carboxylate:



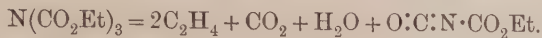
Since the separation of these two substances is difficult, the authors sought a method of decomposition which would yield the latter free from inconvenient by-products, and they found that this object could be attained by heating the tricarboxylic ester with phosphoric oxide.

¹ *Annalen*, 1906, **347**, 233.

² *Ber.*, 1890, **23**, 3505.

³ *Loc. cit.*, 1906, **39**, 1686.

In this case the by-products are ethylene, carbon dioxide, and water:



The foregoing observation led the authors to investigate the action of phosphoric oxide on other esters with the view of ascertaining whether reactions of a similar type could be effected, and with malonic ester they have obtained results of considerable interest.¹

Ethyl malonate was slowly distilled, at a pressure of 12 mm., over a large excess of phosphoric oxide, distributed in glass wool and heated to about 300°; the evolved gases were passed first through a well-cooled tube to remove any unaltered ester, and then into a vessel surrounded by liquid air. The products obtained were ethylene, a little carbon dioxide, and a substance having a very pungent odour, which proves to be a colourless liquid boiling at 7°. By allowing the mixture to boil at the ordinary temperature, the ethylene and carbon dioxide are removed, and the new product is then vaporised and collected in a tube cooled to -60°. It is a very mobile, refractive liquid having an odour resembling that of acetaldehyde or mustard oil. It burns with a smoky blue flame. When treated with cold water it yields malonic acid, and with dry hydrogen chloride, ammonia, and aniline it gives rise to malonyl chloride, malonamide, and malonanilide respectively; it behaves, therefore, as an anhydride of malonic acid. Analysis by combustion with copper oxide and by explosion with oxygen, and molecular weight determination by Hofmann's vapour-density method, show that the compound has the formula C_3O_2 . The authors consider that its formation is represented by the change:



The name carbon suboxide is proposed, and the constitution is represented as $\text{O}:\text{C}:\text{C}:\text{O}$.

The liquid oxide slowly decomposes at the ordinary temperature, being converted after a time into a dark red solid which dissolves in water giving an eosin-red solution; the composition of this product is approximately the same as that of the original liquid. The decomposition is very rapid at 37° and is instantaneous at 100°, and under these conditions carbon monoxide escapes; the solid product which then remains contains less oxygen and is partly soluble in water, giving a brown solution.

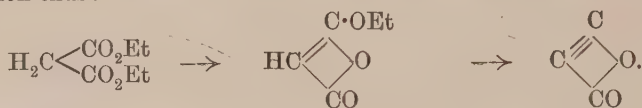
Berthelot² takes exception to the name carbon suboxide, since there appear to be at least three oxides, previously known, to which the name is appropriate. (1) Brodie's oxide, C_4O_3 , obtained by subjecting carbon monoxide to prolonged electric discharges; this might be regarded as an anhydride of tartaric acid. (2) Berthelot's oxide,

¹ *Ber.*, 1906, **39**, 689.

² *Ann. Chim. Phys.*, 1906, **8**, 173.

C_8O_3 , which is formed by heating Brodie's oxide to $300-400^\circ$; in formula this would correspond to an anhydride of dihydroxyphthalic acid. (3) An oxide richer in carbon which results from the action of heat on (2). Berthelot also mentions that in 1891 he gave reasons for suspecting the existence of a volatile lower oxide of carbon, but that owing to the inefficiency of the methods of refrigeration known at that time it was not possible to condense the product.

Michael¹ considers that the constitution assigned to this new oxide by Diels and Wolf is improbable, since in parallel cases the change usually follows an unsymmetric course when the elimination of water occurs with possibility of ring formation. Acetylacetone, for example, yields not an acetylene derivative, but dimethylfuran. For this and other reasons he suggests that the compound should be regarded as the lactone of β -hydroxypropionic acid, and explains its formation thus:



Anhydrides of diethylmalonic acid have been obtained by Einhorn and von Diesbach,² but they prove to be multimolecular. By treating diethylmalonyl chloride with a dilute aqueous solution of pyridine, a yellow amorphous powder is obtained which is dissolved by potassium hydroxide in the cold, giving the salt of diethylmalonic acid. Ammonia converts it into diethylmalonic acid, diethylmalonamide, and diethylmalonamic acid. Analysis and molecular weight determination by the cryoscopic method (in ethylene dibromide) show the formula to be $\left[C(C_2H_5)_2 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} O \right]_{12}$. When this compound is heated in some indifferent solvent, such as benzene, it decomposes, giving carbon dioxide, diethylacetic anhydride, and a crystalline malonic anhydride which behaves towards reagents in the same manner as the original compound, but which has the molecular formula $(C_7H_{10}O_3)_4$.

The methyl ester of dicarboxyaconitic acid,



which was first isolated by Anschütz in 1903, has been further studied by this author and Deschauer.³ It is shown that this ester, when reduced by means of zinc and acetic acid, gives a quantitative yield of methyl dicarboxytricarballoyate,



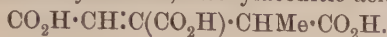
The sodium derivative of dicarboxyaconitic methyl ester reacts with methyl iodide, giving the corresponding methyl derivative; this, when

¹ *Ber.*, 1906, **39**, 1915.

² *Loc. cit.*, 1222.

³ *Annalen*, 1906, **347**, 1.

reduced as before, yields the methyl ester of dicarboxymethyltricarballic acid, $\text{CH}(\text{CO}_2\text{Me})_2 \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CMe}(\text{CO}_2\text{Me})_2$, and when hydrolysed with sodium hydroxide, methyloaconitic acid,



Considerable discussion has taken place with regard to the view put forward by Lewkowitsch in 1900 that the saponification of fats takes place in stages. Balbiano, for example, in 1902—1903 opposed this hypothesis, and considered the change to be of the type $\text{C}_3\text{H}_5(\text{OR})_3 + 3\text{MOH} = \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{MR}$. In support of this opinion he stated that if the saponification of glyceryl tribenzoate is interrupted before the action is complete, the products are only glycerol, benzoic acid, and unaltered tribenzoin, no mono- or di-benzoin being found. Fanto¹ expressed a similar opinion, and was unable to detect the presence of lower glycerides; the reaction, that is, appeared practically to be quadrimolecular. Marcusson also² comes to similar conclusions, and considers that the high acetyl numbers which Lewkowitsch found, and which he himself observes only under certain conditions, are to be explained by the changes experienced by the fatty acids, such as oxydation or anhydride formation. Lewkowitsch, however,³ effectively replies to these criticisms.

Kremann has thrown important light upon this question by making measurements of the reaction velocity in the saponification of glyceryl triacetate and glycoldiacetate. According to Balbiano's view, the first-named reaction should be quadrimolecular and the second termolecular. The values which he obtained, however, were approximately constant when calculated for a bimolecular reaction; if they are calculated on the assumption that the reaction is ter- or quadrimolecular, the numbers increase as the action proceeds. These results appear, therefore, to favour the hypothesis that the change takes place in stages. The rates of saponification of the different acetyl groups differ so little, in the author's opinion, that the effect is analogous to the saponification of the ester of a monohydric alcohol by an equivalent quantity of alkali.

Abel,⁴ reasoning from a kinetic standpoint, proposes to explain the fact that the changes mentioned appear to be reactions of the second order by assuming that the rates of saponification of glyceryl mono-, di-, and tri-acetates are in the ratio of 3 : 2 : 1, and those of glycol mono- and di-acetates in the ratio 2 : 1.

The hydrolysis of esters under the influence of lipase has already

¹ *Monatsh.*, 1904, **25**, 919.

² *Ber.*, 1906, **39**, 3466.

³ *Loc. cit.*, 4095.

⁴ *Zeit., Elektrochem.*, 1906, **12**, 681; and *Zeit., physikal. Chem.*, 1906, **56**, 558.

been the subject of considerable investigation by Kastle and Loevenhart, Armstrong, Nicloux, and others. The enzyme undoubtedly displays a selective power in promoting by preference the hydrolysis of esters of the higher fatty acids, such as those present in the natural fats. The first-named authors (1900) succeeded in effecting the hydrolysis even of the lowest members, but they concluded that the higher the molecular weight of the acid, the more readily is its ethyl ester hydrolysed by lipase. Armstrong and Ormerod¹ have made a further inquiry into the nature of the change, with the object of throwing light on this selective action. Their results lead them to the provisional hypothesis that the hydrolysis of the ester by lipase involves the direct association of the enzyme with the carboxyl centre, and that such association may be prevented by the hydration of this centre. Esters, therefore, which are more attractive of water will be less readily hydrolysed, and this view is in accordance with the fact that the solubilities of ethyl esters diminish as the series is ascended. The influence of hydroxyl replacement is well illustrated by the authors' results obtained with the ethyl esters of succinic, malic, and tartaric acids, the amounts of hydrolysis after twenty-four hours being in the ratio of 20·4 : 15 : 1·8 respectively.

Kastle² states that the alkyl groups—methyl, ethyl, butyl, *isobutyl*, allyl, and benzyl—have almost the same effect on the hydrolysis of esters by (liver) lipase, but that the presence of acyl groups in the homologous series has considerable influence. In the case of methyl propionate the introduction of iodine, in the β -position, tends rather to accelerate than to retard the action, and cyanogen (for example, in cyanoacetic ester) has a retarding influence.

The hydrolysis of nitric esters of glycerol and of cellulose is always a complicated process, owing to the fact that the nitric acid becomes reduced and the alcohol oxidised. Further studies on this subject have been made by Silberrad and Farmer,³ and they show that the hydrolysis of 'nitrocellulose' gives rise to nitric and nitrous acids, ethyl nitrate, ethyl nitrite, alcohol, ammonia, and the following acids: formic, acetic, butyric, dihydroxybutyric, oxalic, tartaric, *isosaccharinic*, and hydroxypyruvic. Carbohydrates and other compounds are also produced. The abnormality of the hydrolysis both of 'nitrocelluloses' and of 'nitroglycerine' is also confirmed by the fact that the amount of alkali consumed on saponification is much higher than that required by theory for the normal change, and further that the velocity of saponification, instead of decreasing normally with the progress of the change, continues to have about the same value until a large proportion

¹ *Proc. Roy. Soc.*, 1906, **78**, 376.

² *Chem. Centr.*, 1906, **i**, 1536.

³ *Trans.*, 1906, **89**, 1182 and 1759.

of the alkali is used up. Intermediate products are probably formed, and these are gradually acted on by the alkali, so that the saponification measured during the later stages is not that of the 'nitrocellulose' alone, but is in part a hydrolysis of decomposition products. No cellulose, or glycerol, is regenerated during these hydrolytic operations, although it can be shown that these substances can resist the action of nitric acid of the concentration present in the experiments. A more active condition of the nitric acid at the moment of its liberation is therefore suggested.

In order to explain the formation of nitrite on the saponification of nitric esters, Nef (1899) assumed that, in addition to the normal reaction, dissociation takes place in the alkyl group with formation of an ethylene and an ethylidene grouping, and that the latter is oxidised to aldehyde by the nitric acid, nitrous acid resulting. Vignon and Maquenne (1891), on the other hand, assumed the formation of an isomeric nitrate, $R \cdot CH(OH)O \cdot NO$. Klason and Carlson¹ now consider that a more probable explanation is afforded by assuming the peroxide formula for the alkyl nitrate, $OR \cdot O \cdot NO$; the changes on saponification might then be represented as $OR \cdot O \cdot NO + KOH = KO \cdot O \cdot NO + ROH$ and $OR \cdot O \cdot NO + KOH = KO \cdot NO + OR \cdot OH$. The formation of an alkyl peroxide in this way appears probable from the authors' experiments, in which nitric esters were saponified in presence of phenyl hydrosulphide, in which cases it is shown that a certain amount of phenyl disulphide is formed. Hydrogen dioxide and other peroxides are known to react with phenyl hydrosulphide with formation of phenyl disulphide, and the authors suggest that the change at present under consideration may take place in the following way: $RO \cdot O \cdot NO + KOH = RO \cdot OH + KO \cdot NO$ and $RO \cdot OH + 2R' \cdot SH = ROH + R'_2S_2 + H_2O$. 'Nitroglycerine,' 'nitrocellulose,' and ethyl nitrate, when saponified under these conditions, all gave rise to some phenyl disulphide.

According to Twitchell,² sulphophenyl- and sulphonaphthyl-stearic acids may act as catalysts in the hydrolysis of fats. A 1 per cent. solution of the latter acid, for example, effects a nearly complete separation of the glycerol from a fat in the course of eight or ten hours.

Busch³ shows that when 'nitrocelluloses' are boiled with alkalis in presence of hydrogen dioxide, the whole of the nitrogen is obtained as nitrate and nitrite. On acidification the nitrite is oxidised by the hydrogen dioxide to nitrate, and the total nitrogen can then be estimated in this state by the "nitron" reagent.

¹ *Ber.*, 1906, **39**, 2752.

² *J. Amer. Chem. Soc.*, 1906, **28**, 196.

³ *Ber.*, 1906, **39**, 1401.

van Romburgh,¹ by acting on glycerol with excess of anhydrous oxalic acid, obtains a product containing 90 per cent. of triformin; diformin yields a similar result when acted on by anhydrous formic acid. When this product is cooled sufficiently, crystals of triformin separate. The pure substance crystallises in needles which melt at 18°. It is slowly hydrolysed by cold water and more rapidly by warm water.

Nitrogen Compounds.

Metallic copper, as is well known, is not dissolved by aqueous ammonia alone; in presence of oxygen, however, the metal is rapidly oxidised and dissolved. At the same time, as shown by Schönbein and by Tuttle, a considerable portion of the ammonia is oxidised to nitrous acid. Extending this observation to organic bases in place of ammonia, Traube and Schönewald² have found that ethylamine is oxidised to acetaldehyde and methylamine to formaldehyde. In these cases the copper is converted to hydroxide, but the ammonia is not oxidised. It is probable that the aldehydes are primarily obtained as aldehyde-ammonias, since the latter do not appear to be acted on by oxygen in presence of metallic copper. When the sodium derivative of glycine is similarly treated the products are nitrous acid and probably glyoxylic acid.

Burmam³ describes a convenient method of preparing methylamine. Commercial methyl sulphate is acted on by 10 per cent. aqueous ammonia and the mixture is afterwards distilled with 30 per cent. caustic soda; the ammonia and methylamine are collected in hydrochloric acid and the resulting hydrochlorides separated by fractional crystallisation.

The preparation of acetamide by the usual method of distilling ammonium acetate gives a comparatively poor yield, since, according to François,⁴ the initial products are ammonia and ammonium hydrogen acetate, the latter then breaking up into acetamide, water, and acetic acid. By starting with ammonium hydrogen acetate, a yield of 45 per cent. of acetamide may be obtained.

For the preparation of amides from esters H. Meyer⁵ recommends digestion of the ester with concentrated aqueous ammonia as the best method, since the action of gaseous or liquefied ammonia may lead to the formation of mixed products. The action of alcoholic ammonia on esters is a reversible process, and if excess of alcohol is present the formation of ester may be the principal reaction even at temperatures below 100°.

¹ *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 109.

² *Ber.*, 1906, **39**, 178.

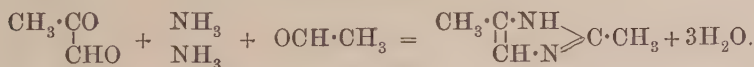
³ *Bull. Soc. chim.*, 1906, [iii], **35**, 801.

⁴ *J. Pharm. Chim.*, 1906, [vi], **23**, 230.

⁵ *Monatsh.*, 1906, **27**, 81.

The methyl esters are much more quickly and completely converted into amides by the action of aqueous ammonia than the higher homologues. On the other hand, the change takes place more readily as the acidic radicle is stronger; trichloroacetic ester, for example, readily gives the amide in this way, whereas trimethylacetic ester does not.

Attention was called in the previous *Report* (1905, 75) to the formation, by Windaus and Knoop, of methylglyoxaline, or methyliminazole, $\text{CH}_3 \cdot \underset{\text{CH} \cdot \text{N}}{\overset{\text{C} \cdot \text{NH}}{\parallel}} > \text{CH}$, from dextrose by the action of ammonia in presence of zinc hydroxide. It was assumed that glyceraldehyde is first formed and that this then passes into methylglyoxal, which in its turn is acted on by ammonia and formaldehyde to give methylglyoxaline. This view is favoured by the fact that a better yield is obtained if formaldehyde is added to the dextrose and zinc hydroxide-ammonia. Since methylglyoxaline occurs in some natural alkaloids it is evident that the synthesis here described may have an important bearing in plant physiology.¹ Windaus² has now extended these observations by the substitution of acetaldehyde for formaldehyde in the above-mentioned synthesis and has in this way obtained 1:4-dimethyliminazole. The change is probably represented as follows:



In absence of acetaldehyde only the mono-methyl base is produced; this appears to indicate that under the conditions here employed acetaldehyde is not formed by the action of hydroxyl ions on dextrose in presence of ammonia.³

In order to establish the constitution of this base advantage was taken of Wallach's observation that the substituted iminazoles in which the replacing radicle is attached to nitrogen are transformed, when led through a red-hot tube, into the 1-substituted compounds. Thus 5-methylglyoxaline yields the 1-methyl compound under these conditions. Now the 1:4(or 5)-dimethylglyoxaline has already been obtained by Jowett and Potter.⁴ By passing this through a strongly heated glass tube and purifying the resulting compound by means of its silver salt, the author obtained a product identical in every way with the 1:4-dimethyliminazole prepared from dextrose and acetaldehyde.

The preparation and synthesis of amino-acids is still receiving considerable attention owing to the importance of these compounds from a

¹ Compare Meldola, *Trans.*, 1906, **89**, 764.

² *Ber.*, 1906, **39**, 3886.

³ Compare Schade, p. 91, this volume.

⁴ *Trans.*, 1903, **83**, 4.

biological standpoint. A complete summary of this subject, bringing the results up to the end of last year, will be found in an address given by Fischer to the German Chemical Society.¹

Of all the known general methods of preparing amino-acids, the simplest appears to consist in the treatment of the α -halogen fatty acid with ammonia. For the purpose of obtaining these halogen derivatives, Fischer and Schmitz² recommend the bromination of the alkyl malonic acids. This method gives a yield of the bromomalonic acid derivative, which is almost quantitative, and the latter on heating readily breaks up into the required bromo-fatty acid and carbon dioxide, especially under diminished pressure. In this way the authors prepared α -bromoisohexoxic acid from isobutylmalonic acid and γ -phenyl- α -bromobutyric acid from γ -phenylethylmalonic acid.

The preparation of amino-acids, through the amino-nitriles, from aldehydes or ketones, may be carried out, as first pointed out by Ljubavin in 1882, by the direct action of ammonium cyanide instead of by the successive treatment with ammonia and hydrogen cyanide; in this way Gulewitsch (1900) obtained a large yield of α -aminoisobutyric acid from acetone. The same author and Wasmus³ make a further study of the most favourable conditions and show that the reaction is of general application for all ketones of the series :



The method has the advantage that iminonitriles and oxynitriles are not produced. Whereas the aminonitriles hitherto described are unstable oils which cannot be distilled, many of those obtained by the present authors could be distilled unchanged, under reduced pressure, and were stable when kept.

Zelinsky and Stadnikoff,⁴ for this preparation, prefer to act on the aldehyde or ketone with potassium cyanide and ammonium chloride, in equal molecular proportion, in aqueous or aqueous-alcoholic solution. They represent the change as taking place in the following way :

(1) $KCN + H_2O \rightleftharpoons KOH + HCN$, (2) $R \cdot CHO + HCN = R \cdot CH(OH) \cdot CN$, (3) $NH_4Cl + KOH = KCl + H_2O + NH_3$, and (4) $R \cdot CH(OH) \cdot CN + NH_3 = R \cdot CH(NH_2) \cdot CN + H_2O$.

For the preparation of amino-acids, the resulting aminonitriles are hydrolysed by means of hydrochloric acid.

Paal and Weidenkaff⁵ have continued their investigations, which were referred to in the previous *Report* (p. 69), on the behaviour of Grignard's reagent towards amino-acids; the investigation was undertaken with the object of obtaining products which might serve for the characterisation of these acids, glycine being first studied. The

¹ *Ber.*, 1906, **39**, 532.

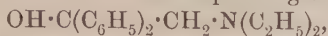
² *Loc. cit.*, 351.

³ *Loc. cit.*, 1181.

⁴ *Loc. cit.*, 1722.

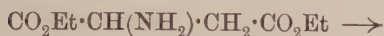
⁵ *Loc. cit.*, 810.

authors now show that the ethyl ester of diethylaminoacetic acid with magnesium ethyl iodide gives rise to diethylaminomethyldiethylcarbinol, $\text{OH}\cdot\text{C}(\text{C}_2\text{H}_5)_2\cdot\text{CH}_2\cdot\text{N}(\text{C}_2\text{H}_5)_2$. This compound, like the product previously described, dissolves easily in organic solvents, but is sparingly soluble in water. The corresponding compound,



is similarly obtained from ethyldiethylaminoacetate and magnesium phenyl bromide.

Extending these observations to aminodicarboxylic acids, the same authors¹ find that the ethyl ester of inactive aspartic acid reacts with magnesium phenyl bromide to give γ - β -amino- $\alpha\alpha\delta\delta$ -tetraphenylbutane- $\alpha\delta$ -diol:



It is a crystalline substance and is very sparingly soluble in water, but dissolves easily in alcohol, ether, benzene, &c.

Siegfried, in 1905, found that on mixing solutions of glycine and barium hydroxide in equivalent quantities and passing carbon dioxide into the mixture, no precipitation of barium carbonate takes place and the clear solution only begins to cloud after standing for some time. Other amino-acids, such as alanine, leucine, aspartic acid, and glutaminic acid, behave in a similar way, and it is shown that the solutions obtained contain salts of corresponding substituted carbamic acids, $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{NH}\cdot\text{CO}_2\text{H}$. Glycine, for example, forms "carbamin-acetic acid," the calcium salt of which has the formula

$$\begin{array}{c} \text{CH}_2\cdot\text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{OCa}\cdot\text{O} \end{array}$$

It would appear that other amphoteric substances, such as peptones and albumoses, can, in presence of bases, form loose compounds with carbon dioxide which are probably of analogous constitution. Even in absence of bases these amino-compounds are capable, to a certain extent, of fixing carbon dioxide.

Leuchs² has now prepared the anhydride, and salts, of carbamin-acetic acid (glycinecarboxylic acid) in an entirely different manner, as follows: carbethoxyglycine is readily converted into its corresponding acid chloride by means of thionyl chloride; on warming this acid chloride for some time at 80° ethyl chloride splits off, leaving the

anhydride, $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{CH}_2\cdot\text{CO} \end{array} > \text{O}$. A better yield is obtained if the carbo-

methoxyglycyl chloride is employed. This anhydride dissolves, giving an acid solution in ice-cold water, but at about 15° carbon dioxide is evolved and pure glycine is left in solution. If the ice-cold aqueous solution of the anhydride is mixed with the calculated quantity of

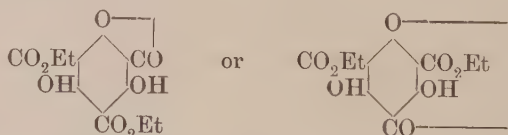
¹ *Ber.*, 1906, **39**, 4344.

² *Loc. cit.*, 857.

baryta-water, a crystalline barium salt is obtained which is found to be identical with the product prepared by Siegfried's method above mentioned.

When the anhydride is rubbed with twice its weight of water at the ordinary temperature it evolves carbon dioxide and is converted into a white, nearly insoluble powder, which appears to be a glycine anhydride $(C_2H_3ON)_x$. This product differs from diketopiperazine¹ and is probably identical with the substance previously obtained by Balbiano and Trasciatti in 1900 by heating glycine with glycerol, and by Curtius from the "biuret base."

The same author² has extended this observation to a study of the behaviour of malonic ester chloride under similar treatment. When this compound was heated at 125—130° for an hour, hydrogen chloride was evolved, but ethyl chloride was not produced; on continuing the reaction, a brownish, horny substance separated, which, after purification by ether, yielded a citron-yellow, crystalline compound having the formula $C_{13}H_{12}O_8$. The author considers that the change which takes place consists in the condensation of three molecules of the ester-chloride, with elimination of hydrogen chloride, to phloroglucinol-tricarboxylic ester, and this, by loss of alcohol, yields the compound in question, which may be



The synthesis of serine was accomplished in 1902 in two different ways by Fischer and Leuchs and by Erlenmeyer, jun., respectively. The first-named authors treated glycollaldehyde, prepared from dihydroxymaleic acid, with hydrogen cyanide and ammonia, and obtained in this way the nitrile of α -amino- β -hydroxypropionic acid; this on hydrolysis gave the corresponding acid, or serine. Erlenmeyer's method consisted in the condensation of the esters of hippuric and formic acids to hydroxymethylenehippuric ester; this on reduction gives rise to benzoylserine, which yields serine on saponification.

Neither of these methods serves well as a method of preparing the substance, and an advantageous new synthesis has now been effected by Leuchs and Geiger³ in which the starting point is commercial chloroacetal. By action of sodium ethoxide on chloroacetal at 120—160°, ethoxyacetal, $CH_2(OC_2H_5) \cdot CH(OC_2H_5)_2$, is obtained, and this by heating with dilute acids yields ethoxyacetaldehyde, $CH_2(OC_2H_5) \cdot CHO$.

¹ Compare *Ann. Report*, 1904, 77.

² *Loc. cit.*, 2641.

³ *Ber.*, 1906, 39, 2644.

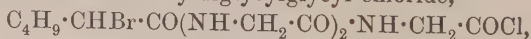
anhydride, $C_6H_{10}O_4N_2$, is obtained. This product is a crystalline, strongly lævrotatory substance, and appears to be identical with a substance which the author has obtained by the hydrolytic decomposition of silk fibroin. From this observation it would appear probable that natural serine is the *l*-compound.

F. Ehrlich¹ states that racemic amino-acids are readily attacked by yeast in solutions containing a relatively large proportion of sugar, and that good yields of *l*-alanine, *d*-leucine, and *l*- α -aminoisovaleric acid were prepared in this way from the corresponding racemic compounds. The yeast appears to attack both optical isomerides, but, in general, one is attacked more rapidly than the other.

Polypeptides.

The researches of Fischer and his colleagues on the chemistry of the polypeptides continue to make a rapid advance. A useful summary of the subject, which includes the results obtained up to the end of 1905, will be found in Fischer's lecture to the German Chemical Society on amino-acids, polypeptides, and proteins, to which reference has already been made. Since that time a large number of highly important results have been obtained, but, in the limited space here available, it would serve no useful purpose to attempt any abstract of this highly detailed and descriptive work.²

As an example of the progress which has been made in the synthesis of peptides containing long chains of amino-acid residues, it may be mentioned, in passing, that Fischer has succeeded in building up a dodecapeptide, containing one leucine and eleven glycine residues. By acting on bromoisohexoyldiglycylglycyl chloride,



with diglycylglycine, $NH_2 \cdot CH_2 \cdot CO \cdot [NH \cdot CH_2 \cdot CO] \cdot NH \cdot CH_2 \cdot CO_2H$, and treating the resulting bromo-compound with ammonia, the heptapeptide leucylpentaglycylglycine,



was obtained. If a similar series of operations is performed with the substitution of triglycylglycine for diglycylglycine, the result is an octapeptide; or, if pentaglycylglycine is employed, a decapeptide. Finally, by proceeding in a similar way with bromoisohexoyltetraglycylglycine chloride and pentaglycylglycine, the dodecapeptide, leucyldecaglycylglycine,



was prepared. In the dry state it has the appearance of a loose, nearly colourless mass, and has no definite melting point. In alkaline

¹ *Zeit. Ver. deut. Zuckerind.*, 1906, 840.

² *Ber.*, 1905, **38**, 4173; 1906, **39**, 453, 530, 752, 2315, 2893, 3981.

solution it gives a strong biuret reaction, and its solution in dilute aqueous ammonia is precipitated by a saturated solution of ammonium sulphate; in most of its properties, in fact, it shows a close resemblance to the natural proteins.

A considerable number of polypeptides containing optically active amino-acid residues have been synthesised and studied; amongst these, *L*-leucylglycine, which was obtained from *d*-*α*-bromoisohexoylglycine and ammonia,¹ yields the anhydride $\text{C}_4\text{H}_9\cdot\text{CH}\cdot\text{NH}\cdot\text{CO}$
 $\text{CO}\cdot\text{NH}\cdot\text{CH}_2$, which is proved to be identical with a product which Fischer and Abderhalden obtained from elastin by hydrolysis with sulphuric acid.²

H. J. H. FENTON.

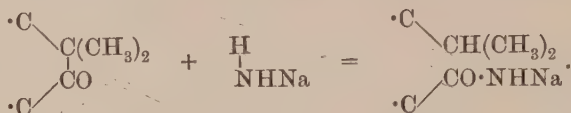
¹ Compare Walden, *Ber.*, 1897, **30**, 3146.

² *Loc. cit.*, 2318.

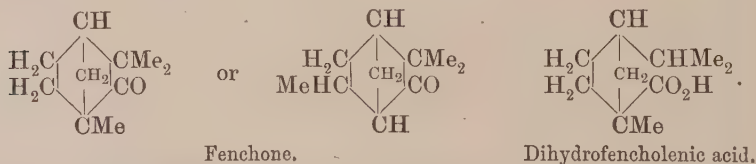
ORGANIC CHEMISTRY—HOMOCYCLIC DIVISION.

Reagents and Reactions.

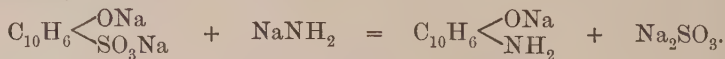
SODAMIDE, which was used by Claisen (*Annual Report*, 1905, 108) as a condensing agent, has been employed by Semmler¹ for breaking down a cyclic ketone wherein a methyl carbon complex adjoins the ketone group:



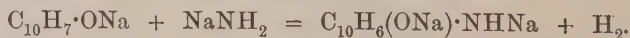
Thus, fenchone gives the amide of dihydrofencholenic acid (*b*), which differs from Mahla's acid (*a*). The following, according to Semmler, represents the relation of fenchone to the acid :



Sachs² and his collaborators in a preliminary paper describe the use of sodamide for preparing aromatic amines from sulphonic acids. A number of naphtholsulphonic acids have been converted into aminonaphthols by fusion of the sodium salt of the sulphonic acid with sodamide,



The 1:5-, 1:8-, and 2:7-naphtholsulphonic acids give good yields of the corresponding aminonaphthols, whilst the 2:6- and 2:8-acids form 1:6-aminonaphthol. As β -naphthol is converted directly into the 1:6-amino-compounds, the above isomeric change appears to result from the rupture of the sulphonic group and the intermediate production of β -naphthol from the two β -naphthol sulphonic acids :



The nitro- and halogen derivatives of benzene give poor yields of

¹ *Ber.*, 1906, **39**, 2577.

² *Ibid.*, 3006.

amino-derivatives ; benzene- and naphthalene-sulphonic acids furnish 30—50 per cent. of the amino-compounds.

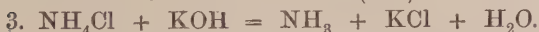
A curious result was obtained by fusing together a mixture of naphthalene, phenol, and sodamide, when α -naphthylamine and 1:5-naphthylenediamine were obtained.

Sodium bisulphite, which Bucherer has already utilised in various ingenious synthetic processes,¹ has now been applied by the same observer² to the preparation of ω -sulphonic acids and ω -cyanides of aromatic amines. The reaction in question consists in acting on the amine with an aldehyde bisulphite and heating the product with potassium cyanide :

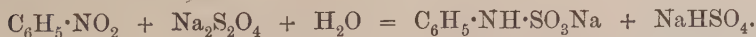


Thus, formaldehyde bisulphite and aniline yield sodium methyl-aniline- ω -sulphonate, $NHPh \cdot CH_2 \cdot SO_3Na$, and ω -cyanomethylaniline, $NHPh \cdot CH_2 \cdot CN$. The importance of this reaction in its connexion with the indigotin synthesis may be realised from the fact that ω -cyanomethylaniline and ω -cyanomethylanthranilic acid can be readily obtained and transformed into the corresponding acids.

The preparation of α -amino-acids, described by Zelinsky and Stadnikoff,³ by the combined action of potassium cyanide, ammonium chloride, and water on aldehydes, although apparently not new (the process was actually patented by Bucherer in 1904), is sufficiently interesting to be reproduced. The changes are explained by the following series of equations :



Seyewetz and Bloch⁴ have employed sodium hyposulphite in presence of sodium phosphate as reducing agent for nitro-compounds, and obtained the sodium sulphonamates of the base. Nitrobenzene gives an equal weight of the sulphonamate, whilst the yield from nitro-toluene is even better :



The action of thiocarbimides on ethylene-aniline and -toluidine has been studied by Davis,⁵ with interesting results. The general character of the products is represented by the following formulæ :



¹ *Ann. Report*, 1904, 86.

² *Ber.*, 1906, **39**, 986, 2796.

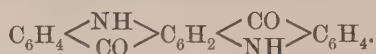
³ *Ibid.*, 1722.

⁴ *Compt. rend.*, 1906, **142**, 1052.

⁵ *Trans.*, 1906, **89**, 713.

the union with one or two molecules of thiocarbimide being determined by the nature of the two reacting substances.

The use of copper referred to in a former Report¹ has been further extended by Ullmann and Maag² to the preparation of *p*-phenylenedianthranilic acid, $C_6H_4(NH \cdot C_6H_4 \cdot CO_2H)_2$, from *p*-dibromobenzene and anthranilic acid dissolved in amyl alcohol in presence of cuprous chloride and finely-divided copper, which are heated together to 140—150°. The product is readily condensed to quinacridone,



A similar method is described by Goldberg³ for converting anthranilic into phenylanthranilic acid, &c. Ullmann and Stein⁴ have also used copper as a catalytic agent for preparing phenyl ethers from phenols and aromatic bromo-compounds. Bromobenzene and guaiacol, or *o*-bromoanisole and phenol, with potassium hydroxide and a trace of copper, yield *o*-methoxydiphenyl ether.

Francis⁵ has shown that benzoyl nitrate, $C_6H_5 \cdot CO \cdot O \cdot NO_2$, obtained by the action of silver nitrate on benzoyl chloride, may be employed as a useful nitrating agent.

Ponzio⁶ finds that sodium hypochlorite converts aromatic aldoximes into diarylglyoxime peroxides of the formula,



Minunni and Ciusa⁷ use amyl nitrate for the same purpose. On the other hand, the chief product of the action of nitrogen peroxide on benzaldoxime, which Scholl described as diphenylglyoxime peroxide, is in reality dinitrophenylmethane, $C_6H_5 \cdot CH : N_2 O_4$. Other aromatic aldoximes give similar products.⁸

A new method of esterification is described by Raikow and Tischkow,⁹ who use syrupy phosphoric acid for effecting the union of alcohol and acid.

Gattermann¹⁰ gives a long and interesting review of the various methods which he has introduced into the preparation of aromatic aldehydes. Some of these have already been described, and include (1) the carbon monoxide method, (2) the hydrogen cyanide method in presence of cuprous or aluminium chloride. The use of organo-magnesium compounds in conjunction with (3) formic ester and (4)

¹ *Ann. Report*, 1905, 102.

² *Ber.*, 1906, **39**, 1693.

³ *Ibid.*, 1691.

⁴ *Ibid.*, 622.

⁵ *Ibid.*, 3798.

⁶ *Atti R. Accad. Sci. Torino*, 1906, **41**, 415; *J. pr. Chem.*, 1906, **73**, 797.

⁷ *Atti R. Accad. Lincei*, 1905, [v], **14**; ii, 518; also Franzen and Zimmermann, *J. pr. Chem.* 1906, **73**, 253.

⁸ *Atti R. Accad. Lincei*, 1906, [v], **15**, 118.

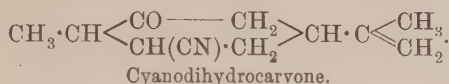
⁹ *Chem. Zeit.*, 1905, **29**, 1268.

¹⁰ *Annalen*, 1906, **347**, 347.

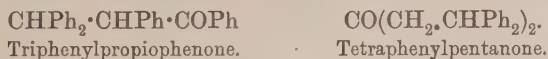
ethoxymethyleneaniline is quite new, and the reactions take place according to the following equations :

1. $\text{CH}_3 \cdot \text{C}_6\text{H}_5 + \text{ClCHO} = \text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{HCl}$.
2. $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_5 + \text{ClCH:NH} = \text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH:NH} + \text{HCl}$.
 $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH:NH} + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{NH}_3$.
3. $\text{RMgBr} + \text{CO}_2\text{H} \cdot \text{C}_2\text{H}_5 = \text{R} \cdot \text{CHO} + \text{C}_2\text{H}_5 \cdot \text{OMgBr}$.
4. $\text{RMgBr} + \text{C}_2\text{H}_5\text{O} \cdot \text{CH:N} \cdot \text{C}_6\text{H}_5 = \text{R} \cdot \text{CH:N} \cdot \text{C}_6\text{H}_5 + \text{C}_2\text{H}_5 \cdot \text{OMgBr}$.
 $\text{R} \cdot \text{CH:N} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O} = \text{R} \cdot \text{CHO} + \text{C}_6\text{H}_5 \cdot \text{NH}_2$

Lapworth¹ has continued his researches on the addition of hydrogen cyanide to unsaturated hydrocarbons (*Annual Report*, 1904, 104), and has prepared cyanodihydrocarvone, which on hydrolysis yields two stereoisomeric carboxylic acids exhibiting dynamic isomerism :



Grignard's Reaction.—This protean synthetic reagent still engages the attention of chemists; but although many papers have appeared on the subject in the past year, few novel applications have been brought to light. Reference may be made to the following: Kohler and his collaborators² have continued their investigations on the action of alkyl and aryl magnesium bromides on unsaturated compounds, and find that the phenyl esters of cinnamic and α -phenylcinnamic acid with magnesium phenyl bromide yield, among a variety of other products, triphenylpropiophenone and tetraphenylpentanone :



With $\alpha\beta$ -unsaturated cyanides,³ additive compounds are formed. Thus, magnesium ethyl bromide and α -phenylcinnamionitrile give two stereoisomeric derivatives according to the equation $\text{CHPh} \cdot \text{CPh} \cdot \text{CN} + \text{Et} \cdot \text{MgBr} + \text{H}_2\text{O} = \text{CHPhEt} \cdot \text{CHPh} \cdot \text{CN} + \text{MgBr} \cdot \text{OH}$.

With magnesium phenyl bromide two products are obtained, namely, an unsaturated k tone and a saturated nitrile :



An interesting method for obtaining esters of alcohols and phenols, which depends on Grignard's reagent, is the subject of a patent by Houben.⁴ It consists in treating the anhydride or acid chloride with the magnesium alkyl halide and the alcohol or phenol. The alcohol is

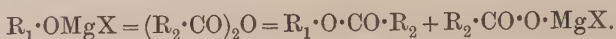
¹ *Trans.*, 1906, **89**, 945.

² Kohler and Heritage, *Amer. Chem. J.*, 1905, **34**, 568.

³ *Amer. Chem. J.*, 1906, **35**, 386.

⁴ *Ber.*, 1906, **39**, 1736.

converted into the halide magnesium alcoholate, which then reacts with the anhydride: .

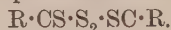


For unsaturated alcohols, magnesium benzyl, methyl, or ethyl chloride were found necessary. In this way esters of linalool, terpineol, thymol, borneol, &c., were obtained.

It is well known that magnesium alkyl and aryl halides unite with carbon dioxide to form acids.¹ Houben² has shown that carbon dioxide can be replaced by carbon disulphide in quite an analogous fashion, forming what the author terms *carbithionic acids*:



They are yellow, red, or violet oils, which are unstable in the free state and have strongly acid properties. They have no tendency to form anhydrides, but easily pass into thioacyl disulphides,



To a similar class of reactions belongs the union of sulphur dioxide with magnesium alkyl halides, which has been investigated by Wuyts and Cosyns,³ and also by Houben and Doescher, and independently by Borsche and Lange.

Houben found that magnesium pinyl chloride, $C_{10}H_{17} \cdot MgCl$, and sulphur dioxide yield dihydropinenesulphinic acid; with sulphur dissolved in toluene, thioborneol⁴ and bornyl disulphide. On fractionating the latter, it decomposed into thioborneol and thiocamphor. Bornyl sulphide, $(C_{10}H_{17})_2S$, was prepared by oxidising thioborneol. Borsche and Lange⁵ obtained thioborneol and the disulphide by the reduction of the sulphonic bromide and subsequent distillation. Wuyts and Cosyns had previously obtained the same thioborneol by the action of sulphur on magnesium phenyl chloride. A reaction not very dissimilar from the above is described by Smiles and Le Rossignol,⁶ in which sulphinic acids are formed by the action of sulphur dioxide on aromatic compounds in presence of aluminium chloride.

Meyer and Tögel⁷ have shown that Grignard's reagent may be applied to the synthesis of ketonic esters by the action of magnesium on a mixture of the acid chloride or bromide and a halogenated ester. Thus, magnesium bromoacetic ester and benzyl bromide gave benzoyl-acetic ester, whilst α -bromopropionic ester yielded β -benzoylpropionic ester.

¹ Grignard, *Ann. Chim. Phys.*, 1901, [vii], **24**, 435; Houben, *Ber.*, 1902, **35**, 2519, 3695; 1903, **36**, 2897; 1905, **38**, 3796.

² *Ber.*, 1906, **39**, 3219.

³ *Bull. Soc. Chim.*, 1903, [iii], **29**, 689.

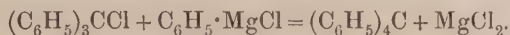
⁴ Wuyts, *Ber.*, 1903, **36**, 869.

⁵ *Ber.*, 1906, **39**, 2346.

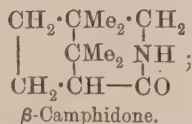
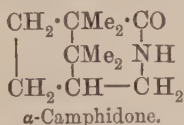
⁶ *Proc.*, 1906, **22**, 158.

⁷ *Annalen*, 1906, **347**, 55.

Gomberg and Cone¹ have used the reagent for obtaining tetraphenylmethane and some of its homologues from triphenylmethyl chloride :

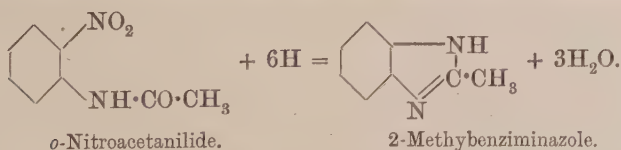


Reduction.—The study of electrolytic reduction of aromatic acids referred to in a previous Report² has been continued by Mettler.³ He uses lead electrodes and an alcoholic sulphuric acid solution of the substance at 20—30°, with a current strength of 6—12 amperes per 100 sq. cm. of surface. In the majority of cases the corresponding alcohols were obtained. Whilst *isophthalic* acid gave the dialcohol, *phthalic* and *terephthalic* acids were converted into dihydro-acids, the former yielding the $\Delta^{3:5}$ -, and the latter the $\Delta^{2:5}$ -acid. Electrolytic reduction has also been applied to camphoric imide by Tafel and Bublitz,⁴ who obtained two isomeric α - and β -camphidones to which they assign the following formulæ :



and also to camphorcarboxylic acid by Brecht,⁵ who obtained borneol-carboxylic acid.

Brand,⁶ who has applied the electrolytic method to aromatic polynitro-compounds, obtained nitrohydroxylamino- and nitro-azoxy-compounds; *o*-nitroacetanilide⁷ in alkaline solution gave *o*-azoacetanilide together with traces of the azoxy-compound, in mineral acid solution, *o*-phenylenediamine and in acetic acid solution 2-methylbenziminazole.



Among other reducing agents which have been studied in conjunction with polynitro-compounds is hydroxylamine in alkaline solution, which has been introduced by Meisenheimer. The results obtained by Meisenheimer and Patzig⁸ with *o*- and *p*-dinitro-compounds indicate the formation of diaci-dinitro-dihydrobenzene. For example, *o*- and *p*-dinitrobenzene react in the following way :



the products on acidifying pass into the nitronitroso-compounds.

¹ *Ber.*, 1906, **39**, 1461.

³ *Ber.*, 1906, **39**, 2933.

⁵ *Annalen*, 1906, **348**, 199.

⁷ Brand and Stohr, *Ber.*, 1906, **39**, 4058.

² *Ann. Report*, 1905, 106.

⁴ *Ibid.*, 1905, **38**, 3806.

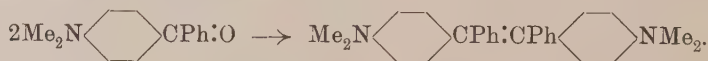
⁶ *Ber.*, 1905, **38**, 4006.

⁸ *Ber.*, 1906, **39**, 2526, 2533.

The *m*-dinitrobenzene behaves quite differently, and yields a *m*-dinitro-*m*-phenylenediamine as the result of a long series of changes described by the authors in the original memoir.

Grandmougin¹ finds sodium hyposulphite to be an active reducing agent for azo-, nitro-, and nitroazo-compounds; also for quinones and diketones like benzil, the latter being converted into hydrobenzoin.

An interesting case of reduction is described by Willstätter and Goldmann,² in which the amino-derivatives of benzophenone on reduction with tin and hydrochloric acid undergo condensation into ethylene derivatives. *p*-Dimethylaminobenzophenone, for example, yields tetramethyldiaminotetraphenylethylene:



A very important case of reduction is one described by Semmler,³ in which he shows that γ -, δ -, and ϵ -glycols can be readily obtained from the corresponding lactones by reduction with sodium in alcoholic solution.

Oxidation.—Harries⁴ has continued his study of the action of ozone on organic compounds. He shows that unsaturated alcohols as well as unsaturated hydrocarbons combine with a molecule of ozone and form ozonides. On the other hand, unsaturated ketones, aldehydes, and monobasic acids take up four atoms of oxygen, one molecule of ozone attaching itself to the double link C:C and the fourth atom of oxygen to the carbonyl group C:O. The structure of the latter group of ozonides and their decomposition by water may be illustrated in the case of the ozonide of mesityl oxide:



The acetone peroxide which is formed subsequently breaks up by the action of another molecule of water into acetone and hydrogen peroxide. The author sums up the action of ozone under two heads: the molecule of ozone either attaches itself as O₃ and forms an ozonide, or it breaks up and yields a labile peroxide. The ozonide method has been utilised for obtaining a variety of rare preparations, such as levulinaldehyde, as well as for ascertaining structure.

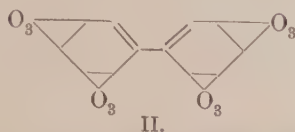
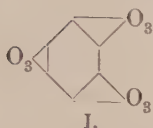
In this connexion the formation of a triozone of benzene (I) and a tetraozonide of diphenyl (II) is cited in opposition to the centric formula for benzene. Naphthalene (III), on the other hand, gives a diozone, and indicates therefore a difference in the structure of the two nuclei:

¹ Ber., 1906, 39, 3561, 3929.

² Ibid., 3765.

³ Ibid., 2851.

⁴ Annalen, 1906, 343, 311.

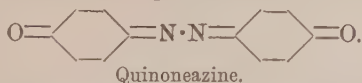


In a later paper¹ Harries and Neresheimer point out that the unsaturated hydroaromatic compounds are sharply distinguished from the open chain compounds and members of the aromatic series by their stability in presence of water. Tetrahydrobenzeneozonide, to take one example, is obtained as a white jelly-like mass, which becomes powdery on washing with ether, and is only decomposed on long boiling with water, when it is transformed into *n*-adipic acid and a small amount of the corresponding aldehyde.

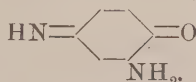
The oxidation of phenols and amines by means of silver oxide,² which has led to such interesting results in the hands of Willstätter and his co-workers, has been the subject of further study.³ In the present case benzidine, dihydroxystilbene, and the azophenols have been selected for investigation. It has already been stated that benzidine in indifferent solvents yields an oxidation product. This has now been synthesised and identified, not as diphenylquinonedimine (Annual Report, 1905, 128), but as diaminoazodiphenyl:



The formation takes place apparently through diphenoquinonedimine, which then polymerises, the process being marked by various colour changes. *p*-Azophenol is oxidised by silver oxide or lead peroxide in ethereal solution to quinoneazine:



It has a deep orange-red colour. On reduction it changes into a new modification of *p*-azophenol, which the author regards as a geometrical isomeride of the original compound. *o*- and *m*-Azophenol are not oxidised by silver oxide, nor is *p*-azoaniline, but *p*-dihydroxystilbene is converted into stilbenequinone. Kehrman and Prager⁴ have used ferric chloride in aqueous solution for oxidising aminophenols, and obtained quinoneimines. For example, 2:4-diaminophenol yields 2-amino-1:4-benzoquinoneimine which was precipitated as dichromate and picrate, but was not isolated:



2-Amino-1:4-benzoquinoneimine.

¹ Ber., 1906, 39, 2846.

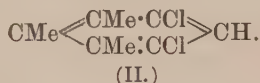
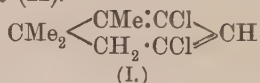
² Ann. Report, 1904, 122; 1905, 127.

³ Ber., 1906, 39, 3474, 3482, 3492.

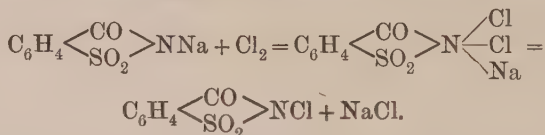
⁴ Ibid., 3437.

In a further study of the structure of the aromatic purpuric acids, Borsche and Gahrtz¹ have oxidised the products of the action of potassium cyanide on polynitrophenols with potassium hypobromite, and obtained a series of nitrocyanophenols.

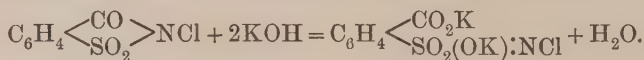
Chlorination.—The researches connected with chlorination and bromination have followed former lines. Crossley and Hills² have studied the action of phosphorus pentachloride on trimethyldihydroresorcin, which yields 3:5-dichloro-1:1:2-trimethyl- $\Delta^{2:4}$ -dihydrobenzene (I) and, by loss of hydrogen, 3:5-dichloro-1:2:6-trimethylbenzene (II).



Chattaway³ by passing chlorine into an alkaline solution of saccharin obtained one or other of two products, determined by the quantity of alkali present. The changes are indicated as follows:



The latter then breaks up in presence of excess of alkali:



A research on the chlorination of the substituted oxamides⁴ has yielded results not very dissimilar from those obtained by the chlorination of the anilides, &c., already reported.

A continuation of Zincke's investigation⁵ on the action of bromine and chlorine on phenols⁶ is too long to be satisfactorily curtailed, and the reader is therefore referred to the original papers.

An interesting series of additive compounds with the halogens and halogen acids is described by Hantzsch and Denstorff.⁷ The series is divided into two groups named *perhaloids*, containing bromine and iodine, and *hydrogen perhaloids*, containing a certain number of molecules of hydrogen bromide and iodide. Among the former the best characterised is the tetraiodide of α -diethoxydinaphthastilbene and the dibromide of the same compound,



Dixanthylene apparently gives products up to the decaiodide.

¹ *Ber.*, 1906, **39**, 3359.

² *Trans.*, 1906, **89**, 875.

³ *Ibid.*, 1905, **87**, 1882.

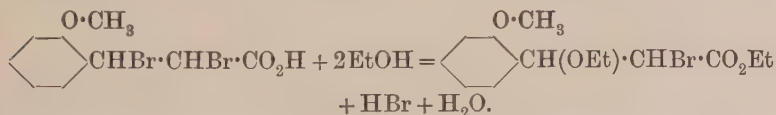
⁴ *Ibid.*, 1906, **89**, 155.

⁵ *Annalen*, 1906, **343**, 75, 100; **349**, 67 *et seq.*

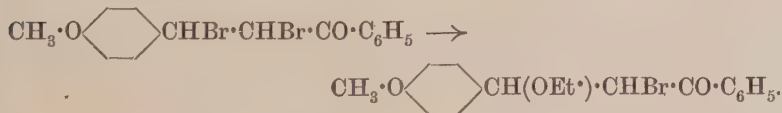
⁶ *Ann. Report*, 1904, 95.

⁷ *Annalen*, 1906, **349**, 1.

Dibenzylideneacetone gives an additive product which contains hydrogen iodide and iodine ($C_{17}H_{14}O$)₂, HI_5 , and dimethylpyrone forms a compound, $(C_7H_5O_2)_2, HBr_3$. They are precipitated by mixing solutions of the constituent substances as dark-coloured, amorphous compounds, which can also be obtained in the crystalline condition. The union of the halogen and halogen acid is a very feeble one, and appears to be partly broken by solution in indifferent solvents. Nevertheless, the cryoscopic results point to the actual existence of these compounds in solution. A. Werner¹ has studied the behaviour of aromatic dibromides (containing bromine in the side chain) towards alcohols and phenols, and found that an ortho- or para-methoxyl group greatly enhances the reactivity of the α -bromine atom, so that by warming with the alcohol or phenol the bromine is replaced. Thus, *o*-methoxycinnamic dibromide and ethyl alcohol combine as follows :



Anisylideneacetophenone dibromide shows a similar behaviour :



The difference in reactivity is manifest by comparison with the dibromide of cinnamic acid, which is not affected by alcohol.

Diazotisation.—An interesting case of steric hindrance in connexion with the diazo-reaction is recorded by Schmidt and Schall,² who find that whilst the 4-aminodiphenic acid is readily diazotised, only one of the amino-groups in the 6:6'-diamino-acid is attacked, whilst the 6-aminodiphenic acid cannot be diazotised :



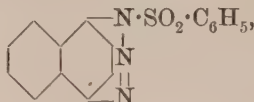
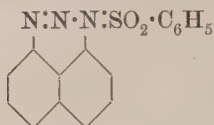
Morgan and Micklethwait³ have attempted to ascertain the structure of the *p*-diazoimino-compounds described in the *Annual Report* for last year (p. 108) by studying the constitution of the diazo-compound from benzenesulphonyl-1:8-naphthylenediamine. They conclude that the

¹ *Ber.*, 1906, **39**, 27.

² *Ibid.*, 1905, **38**, 3769.

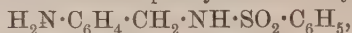
³ *Trans.*, 1906, **89**, 4 ; *Ber.*, 1906, **39**, 2869.

similarity between this and the *p*-diazimide, previously obtained, points to similarity in structure, which they represent as follows :

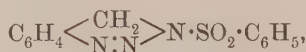


in preference to the iminodiazide formula which was suggested as a possible alternative. No anhydride formation of this character has been observed with the sulphonyl derivatives of *m*-diamines.¹

The study of the action of nitrous acid on the mixed aliphatic and aromatic bases like ω -benzenesulphonylaminobenzylamine,

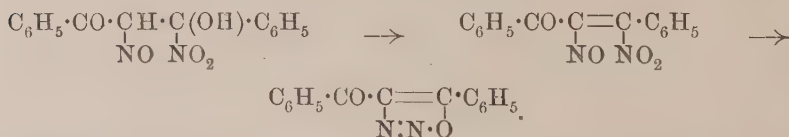


has disclosed the fact that both ortho- and meta-compounds (the latter much less readily) yield diazoimides, whereas the para-compounds do not. The diazoimino-formation depends on the presence of hydrogen in the group $\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$,

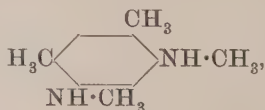


for if it is replaced no anhydride formation occurs.

The structure of the compound obtained by the action of nitrous acid on dibenzoylmethane, which was previously described by Wieland and Bloch,² has now been identified by them³ as a diazoanhydride, and is probably formed in the following way :



A further contribution by Morgan and Clayton⁴ on the influence of substitution on the formation of diazoamines and aminoazo-compounds studied in the case of *s*-dimethyl-4 : 6-diamino-*m*-xylene,



serves to confirm previous observations that dimethylation of both symmetrical and unsymmetrical amino-groups of a dipara-substituted *m*-diamine greatly retards but does not entirely prevent the introduction of a diazo-complex into the aromatic nucleus of a diamine.

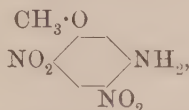
¹ *Trans.*, 1906, **89**, 1289.

³ *Ibid.*, 1906, **39**, 1488.

² *Ber.*, 1904, **37**, 1524, 2524.

⁴ *Trans.*, 1906, **89**, 1054.

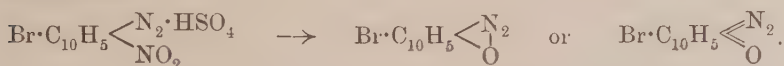
Meldola and Stephens,¹ in continuation of former work (*Annual Report*, 1905, 106) on the removal of nitro- and methyl-groups in the course of diazotisation, show that since 4 : 6-dinitro-*m*-anisidine,



4 : 6-Dinitro-*m*-anisidine.

behaves normally, the rupture of the nitro-group depends on the ortho and para position of the diazonium group, and on the presence of a similar group in the adjacent position.

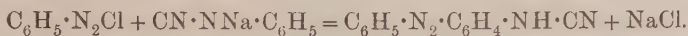
A further study of diazotisation by Meldola and Dale² has shown that 4-bromo-2-nitro-1-naphthylamine, when diazotised in sulphuric acid solution, diluted and heated, loses a nitro-group and passes into a diazo-oxide :



The action of diazohydrates on oximes is the subject of a research by Mai and his collaborators,³ in which a series of condensation products of one molecule of diazo-compound with two of the oxime has been obtained.

A new method is described by Silberrad and Smart⁴ for obtaining bistriazobenzene, by which in the place of *p*-phenylenediamine the *p*-acetyl derivative is diazotised and converted successively into the acetyl-*p*-aminotriazobenzene and *p*-aminotriazobenzene, and finally into the perbromide and the bistriazo-compound.

A group of aromatic cyanamides are described by Pierron,⁵ who obtains them by the action of a neutral diazobenzene salt on a primary cyanamide :



They are acid substances, form alkali salts, take up water in acid solution, passing into carbamides, and break up on reduction into aromatic amines and *p*-aminocarbamides.

Condensation.

Among the products of condensation which have latterly attracted attention are the so-called *fulgenic acids* and *fulgides* of Stobbe and his collaborators. The results of their investigations are contained in a series of papers which have appeared since 1904, and to which a

¹ *Trans.*, 1906, **89**, 923.

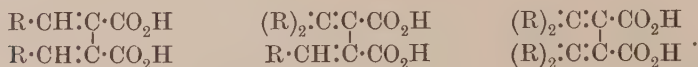
² *Proc.*, 1906, **22**, 156.

³ *Ber.*, 1906, **39**, 876.

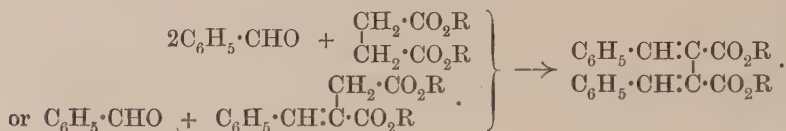
⁴ *Trans.*, 1906, **89**, 170.

⁵ *Compt. rend.*, 1906, **143**, 340.

brief reference has already been made in last year's *Annual Report*.¹ The subject has attained some importance in view of the present uncertain nature of the relation existing between colour and structure. The fulgenic acids are derivatives of succinic acid, the fulgide of its anhydride, and possess the following general structure (R = aryl or alkyl):



They are obtained by condensing aldehydes with succinic ester, or with γ -mono-substituted itaconic esters, thus:



The tri- and tetra-substituted derivatives are obtained in a similar manner, using ketones and aldehydes in place of aldehydes alone.

The fulgenic acids are crystalline substances which are faintly orange or yellow in colour. The acids are readily converted into the anhydrides or fulgides by fusion or by the action of acetyl chloride in the cold. They are well-crystallised compounds of a red, orange-yellow, yellowish-green, and brown colour, which exhibit metallic lustre and occasionally marked pleochroism. The colour is closely associated with the nature of the radicles present. The anhydrides are converted by alkalis into the corresponding faintly-coloured acids, passing in the process through an intermediate coloured stage. The fulgides are affected by heat and light, some of them when exposed to bright light changing into highly coloured products, and reverting to the original colour in diffused light. The reversible change becomes less and less marked with each successive transformation, whilst the orange or yellow colour becomes paler, until a final condition is reached which represents a new isomeric compound. Similar reversible colour changes are produced by heat, with the formation of the same isomeric substances.

But the chief interest connected with these compounds lies in the colour change effected by the presence of different radicles. Thus, the tetramethylfulgide is colourless, the phenyltrimethyl compound is sulphur-yellow, the phenyl, diphenyl, and dimethyl compounds are orange-yellow, whilst the tri- and tetra-phenyl derivatives are orange-red and blood-red respectively.² Similar results have been experienced with other substituents, that is to say, the alkylfulgides

¹ *Ann. Report*, 1905, 158.

² *Ber.*, 1905, 38, 3673.

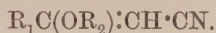
are colourless and the aryl derivatives are coloured, the colour deepening with the number of aryl radicles.¹ The introduction of a furyl group in place of phenyl intensifies the tint still more; thus diphenyl-furylfulgide is dichromate-red compared with triphenylfulgide, which is orange-red.² The *o*- and *m*-nitrophenyl groups also produce a deeper colour than the unsubstituted phenyl group, whilst the *p*-nitro-group has the reverse effect and lightens the tint.³ The methoxyl group in the phenyl radicle also intensifies the colour.⁴

The reader is referred to the section on colour and structure (p. 143), in which the above results appear to harmonise well with the views of Hartley and v. Baeyer.

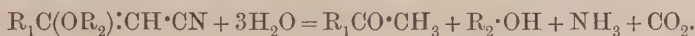
An interesting case of condensation is that of ethyl α -chloropropionate with aldehydes, which has been studied by Darzens.⁵

Glycidic esters of the formula $\text{O} \begin{array}{c} \text{CMe} \cdot \text{CO}_2\text{Et} \\ \diagup \quad \diagdown \\ \text{CHR} \end{array}$ are formed, the yield being greater in the case of aromatic than of the aliphatic members.

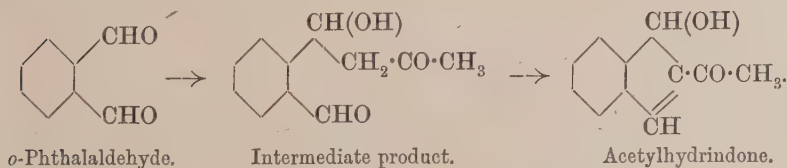
Moureu and Lazennec⁶ have succeeded in preparing acetylenic nitriles of the formula $\text{R} \cdot \text{C} \vdash \text{C} \cdot \text{CN}$ from the corresponding esters and amides by distilling the latter with phosphorus pentoxide. These substances can be used for obtaining β -alkyloxy and aryl-acrylic nitriles by condensation with alcohols and phenols:



They break up on hydrolysis into a ketone as follows:



The products of condensation of *o*-phthalaldehyde with other substances has been studied by Thiele and Falk.⁷ They find that ring-formation usually follows, except in the case of Perkin's reaction, which in the case of acetic acid gives *o*-phenylenediacyrylic acid, $\text{C}_6\text{H}_4(\text{CH} \vdash \text{CH} \cdot \text{CO}_2\text{H})_2$, and phenylhydrazine, which yields a dihydrazone. Acetone forms 2-acetyl-3-hydrindone, and acetophenone the corresponding benzoylhydrindone:



¹ *Ber.*, 1905, **38**, 3897.

² *Ibid.*, 4075.

³ *Ibid.*, 4081; 1906, **39**, 392.

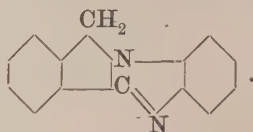
⁴ *Ibid.*, 761.

⁵ *Compt. rend.*, 1906, **142**, 214.

⁶ *Ibid.*, 211, 338, 450.

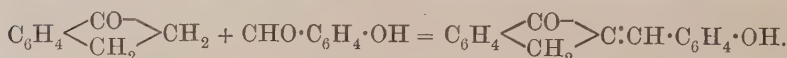
⁷ *Annalen*, 1906, **347**, 112.

Also *o*-phenylenediamine condenses to *o*-benzylenebenziminazole :

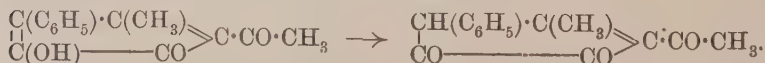


Perkin, jun., and Robinson¹ have condensed α -hydrindone and 4:5-dimethoxy- α -hydrindone with salicylaldehyde and *p*-methoxysalicylaldehyde, with the object of elucidating the structure of certain brazilin and hæmatoxylin derivatives.

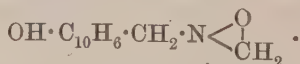
α -Hydrindone and salicylaldehyde undergo condensation as follows :



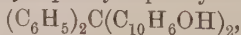
A continuation of the former researches on the condensation of phenylpropiolyl chloride with sodium acetylacetone by Ruhemann² has served to confirm the previous formula assigned to the red compound obtained.³ The transformation from the red compound to a colourless derivative by union with phenylhydrazine, semicarbazide, and hydroxylamine indicates, according to the author, an intramolecular change of the following character :



Betti has shown that β -naphthol and formaldehyde condense together with ammonia.⁴ By replacing ammonia by hydroxylamine he now obtains a compound to which the following formula is assigned :⁵

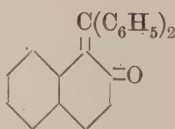
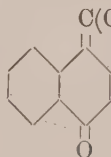


Clough⁶ has condensed benzophenone chloride with α - and β -naphthol and obtained di- α -hydroxynaphthyldiphenylmethane,



and di- β -naphthoxydiphenylmethane, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OC}_{10}\text{H}_7)_2$, respectively.

With the sodium salts of the two naphthols, compounds of the following formulæ were obtained :



¹ *Proc.*, 1906, **22**, 160.

³ *Trans.*, 1906, **89**, 682.

⁵ *Gazzetta*, 1906, **36**, i, 388.

² *Ann. Report*, 1905, 147.

⁴ *Ann. Report*, 1904, 99.

⁶ *Trans.*, 1906, **89**, 771.

Isomeric Change.

There are few interesting cases of isomeric change to be recorded during the past year. Klages and Kessler¹ have continued a former investigation² on the isomeric change of ethylene oxides, and show that diphenylethylene oxide by distillation under low pressure or by boiling with concentrated bisulphite solution passes into diphenylacetaldehyde :

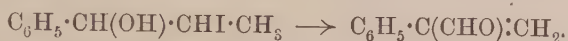


The same result has been arrived at by Tiffeneau³ by boiling $\beta\beta$ -diphenylethylene glycol with 20 per cent. sulphuric acid, whereas the diphenylglycol iodohydrin $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH}) \cdot \text{CH}_2\text{I}$ gives desoxybenzoin.

A similar result was obtained with α -phenylpropylene- $\alpha\beta$ -glycol, which gives phenylacetone on boiling with dilute sulphuric acid,



whilst the iodohydrin is transformed by intramolecular change into atropaldehyde :

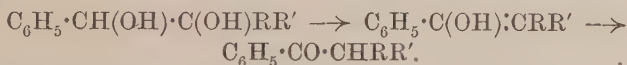


On the other hand, both phenylethyleneglycol and its iodohydrin, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{I}$, give phenylacetaldehyde.

In a further communication on the subject,⁴ Tiffeneau and Dorlencourt show that the molecular changes involved in the conversion of hydrobenzoin into diphenylacetaldehyde and similar transformations depend on the stability of the hydroxyl in proximity to the phenyl group; for in γ -ethylpentylene- $\beta\gamma$ -glycol, and $\alpha\alpha$ -diphenylpropylene- $\alpha\beta$ -glycol, in which a hydroxyl is vicinal to an alkyl group, ketones are formed and no interchange of radicles occurs,



whilst methyl- and ethyl-hydrobenzoin change as follows :



Thus, the hydroxyl is stable in juxtaposition to the phenyl group, and where both hydroxyls occupy this position and are therefore stable, a more fundamental change follows and a shifting of radicles occurs.

A long paper on a similar topic has also been published by Stoermer.⁵

¹ *Ber.*, 1906, **39**, 1753.

² *Ann. Report*, 1905, 112.

³ *Compt. rend.*, 1906, **142**, 1537.

⁴ *Ibid.*, 1906, **143**, 126.

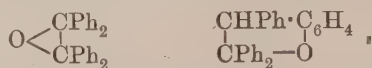
⁵ *Ber.*, 1906, **39**, 2288.

The author's object was to obtain glycol ethers, to convert them by hydrolysis into the corresponding glycols, and then by removal of water into aldehydes. The preparation of the glycol ethers was effected by Grignard's method from ethyl phenoxy- and ethoxy-acetates. The conversion into aldehydes by boiling with dilute sulphuric acid occurred much more readily with the ethoxy- than with the phenoxy-derivatives. The author found the phenoxyl could be replaced by the ethoxyl group by boiling the former compound with alcoholic potassium hydroxide under pressure. For example, diphenyl-phenoxyethylcarbinol from ethyl phenoxyacetate and magnesium phenyl bromide on boiling with alcoholic potash gave the corresponding ethoxy-compound,



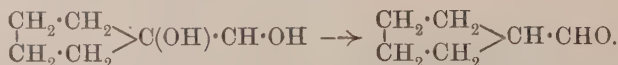
and on decomposition with 20 per cent. sulphuric acid, diphenyl-acetaldehyde. In this way a series of both aromatic and aliphatic aldehydes was prepared.

The above changes are clearly associated with the pinacone-pinacolin conversion referred to in the *Annual Report* of last year,¹ a process which has been submitted to further investigation by Delacre² without leading to any definite result. The structure of α - and β -benzo-pinacolins has also been the subject of a fresh investigation by Wertheimer³ and also by Delacre.⁴ Whilst the former considers both compounds to be oxides of the following formulæ,



Delacre is of opinion that the structure of neither is fully established.

To the same order of phenomena belongs Wallach's observation⁵ of the conversion of *cyclopentane* glycol by heating with dilute sulphuric acid into *cyclopentane*aldehyde :



Another interesting case of isomeric change is described by Johnson and Jamieson.⁶ They find that the benzoyl derivatives of unsymmetrical Ψ -methyl- and Ψ -ethyl-thiocarbamides pass, on boiling their alcoholic solutions, or by heating them above their melting points, into the stable symmetrical compounds :



¹ *Ann. Report*, 1905, 110.

³ *Monatsh.*, 1906, **26**, 1533.

⁵ *Annalen*, 1906, **347**, 316.

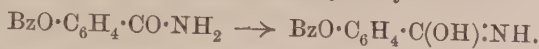
² *Bull. Soc. chim.*, 1906, [iii], **35**, 343.

⁴ *Bull. Acad. Roy. Belg.*, 1906, 7.

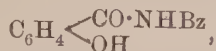
⁶ *Amer. Chem. J.*, 1906, **35**, 297.

The two classes of compounds are easily distinguished by their behaviour with alkalis and hydrochloric acid. The former are decomposed by alkalis into monobenzyl- ψ -carbamides and benzoic acid, whereas the latter are dissolved and precipitated by acids unchanged. On boiling with hydrochloric acid they are decomposed into mercaptans and dibenzoylcarbamides.

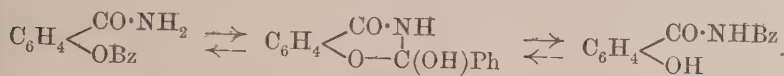
Titherley and Hicks¹ last year isolated two benzoyl derivatives of salicylamide, the one melting at 144° readily changing into the other melting at 208°. The relation between the two compounds was then expressed by the amide and imino-hydroxy-formulae:



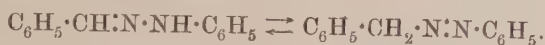
This view was contested by Auwers. The authors² now suggest another interpretation, according to which the more stable compound melting at 208° has the following constitution:



and its conversion into the more labile compound on the one hand and into the *N*-ester on the other is brought about by a series of reversible changes:



Finally, mention should be made of the action of light on benzaldehydephenylhydrazone, which, according to Chattaway,³ changes into the isomeric azo-compound



Unsaturated Compounds.

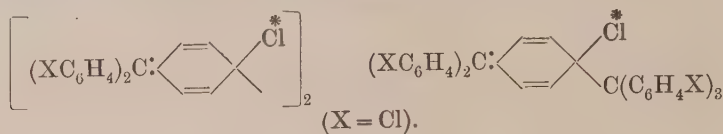
Gomberg and Cone⁴ return to the discussion of the structure of triphenylmethyl, to which reference has already been made.⁵ They discard the hexaphenylethane theory, on the ground that both tetra- and penta-phenylethane are entirely stable substances, and there is no reason for assuming that hexaphenylethane should differ in this respect from the other two. The oxidisability and reactivity with iodine exhibited by triphenylmethyl are opposed to the stability which one would infer from a union between two nuclei as represented in the quinonoid formulae of Heintschel and Jacobson. If either formula is correct, it should manifest itself by the behaviour of the *p*-halogen

¹ *Trans.*, 1905, **87**, 1207. ² *Ibid.*, 1906, **89**, 1318. ³ *Proc.*, 1906, **22**, 36.

⁴ *Ber.*, 1906, **39**, 3274.

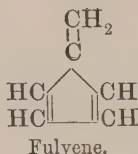
⁵ *Ann. Report*, 1905, 117.

derivatives of triphenylmethyl. The formulæ of Heintschel and Jacobson would represent these substances as follows :



In both cases the chlorine atom in the quinone nucleus, indicated by the asterisk, should be removable by zinc or silver, thereby linking together two molecules of the original compound. The authors have submitted this view to a critical experimental examination by studying the behaviour of a series of halogen derivatives of triphenylchloromethane. From the results, which can only be traced here in outline, they consider that the problem is not yet definitely solved. The coloured products, which are formed by the removal of the "carbinol-chlorine" with molecular silver from the haloid derivatives of triphenylchloromethane, must possess the same structure as triphenylmethyl, since they all give peroxides under similar conditions; but this structure cannot be represented by $(\text{XC}_6\text{H}_4)_3\text{C}$ —that is, as a derivative of triphenylmethyl—since it assigns the same function to all three phenyl groups. This cannot be the case, as they show that the halogen of one of the phenyl groups is removable, and therefore one phenyl group possesses a different function from the other two. They attribute this to the probable presence of a quinonoid structure of some kind, but different from either of those proposed, and consider the coloured products obtained by the removal of halogen to be related to the triphenylmethane dyes.

Thiele and Bühner¹ have studied the reducing action of the aluminium-mercury couple on certain fulvene derivatives. These unsaturated hydrocarbons were first obtained by Marckwald² by condensing aldehydes with indene. They have a yellow colour, and are regarded as derivatives of the hypothetical hydrocarbon named fulvene :

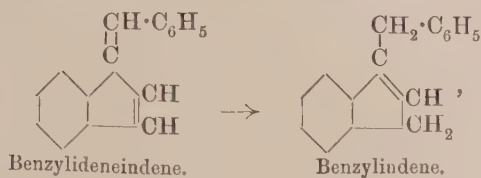


The authors find that reduction with the couple takes place readily if there is a phenyl or carboxyl group attached to the unsaturated carbon group outside the ring, and at the same time the yellow colour

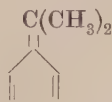
¹ *Annalen*, 1906, **347**, 249 ; **348**, 1.

² *Ber.*, 1895, **28**, 1501.

vanishes. Thus, yellow benzylideneindene yields colourless benzylindene,



whereas dimethylfulvene is not reducible :



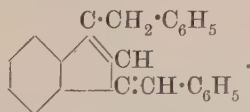
Dimethylfulvene.

The reducibility also appears to depend on the presence of the *cyclopentadiene* ring, for whilst bisdiphenylene-ethylene (I) is reducible, tetraphenylethylene (II) is not :

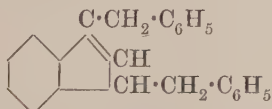


The result thus contradicts H. Wislicenus's rule that the couple is not adapted to the reduction of aromatic nuclei or double bonds in open carbon chains.

Where reduction occurs with a conjugated double bond the addition of hydrogen usually, although not invariably, follows Thiele's rule.¹ The authors find further that benzylindene undergoes condensation with benzaldehyde, yielding a yellow hydrocarbon to which they assign the formula of benzylbenzylideneindene :

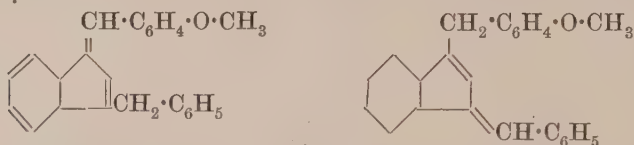


This hydrocarbon also takes up hydrogen on reduction, and gives a colourless product of the formula :

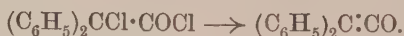


¹ *Ann. Report*, 1904, 105.

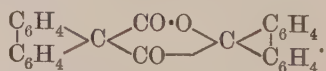
A further interesting outcome of this research is the proof that benzylindene obtained by Thiele, as described above, and Marckwald's benzylindene, prepared by direct benzylation of indene, are identical, and that the same is true of the reduction products of benzyanisylideneindene and anisylbenzylideneindene, the first of which is obtained by condensing benzylindene with anisaldehyde, and the second by condensing anisylindene with benzaldehyde. The identity of these pairs of compounds is explained by the presence of an "oscillating double bond":



An interesting class of new compounds was described last year by Staudinger¹ under the name of *ketenes*, having the general formula $\text{R}_2\text{C}:\text{CO}$. They have since been the object of further study.² Diphenylketene is obtained by the action of zinc filings on chlorodiphenylacetyl chloride,



Diphenyleneketene is prepared in a similar fashion from chlorodiphenyleneacetyl chloride, and in properties resembles diphenylketene. It is a yellow crystalline compound, which melts at $90-90.5^\circ$ and decomposes in a vacuum at 150° . It is extremely sensitive to water, combining with it and forming diphenylene-acetic acid, and with alcohol forming the corresponding ester. It also combines with aniline to form the anilide, and with phenylhydrazine to form the hydrazide. If the precipitate of zinc chloride and ketene obtained in the course of its preparation is exposed to the air, a new compound is produced, to which the author assigns the following formula:



The investigations of Posner, referred to in last year's *Report*, (p. 115) on the behaviour of unsaturated compounds have been continued.³ In the present case the author has studied the union of hydroxylamine with cinnamic and *p*-methylcinnamic acids, and obtained β -hydroxylaminophenylpropionic acid, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{NH} \cdot \text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, and the corresponding *p*-tolyl compound. A number of their derivatives are described and their structure discussed. The preparation of α -chlorocinnamic and chloro*allocinnamic* acids is described by Sudborough and James.⁴ Both compounds are formed from

¹ *Ber.*, 1905, **38**, 1735.

² *Ibid.*, 1906, **39**, 3062.

³ *Ibid.*, 3515, 3705.

⁴ *Trans.*, 1906, **89**, 105.

$\alpha\beta$ -dichloro- β -phenylpropionic acid by removal of hydrogen chloride with alkali, and the acids are subsequently separated by crystallisation of the barium salts in a similar fashion to the bromine derivatives. The conditions of interconversion of the *allo*-acid and its isomeride are discussed.

Derivatives of Hydrocarbons with Condensed Nuclei.

Among the multitude of new naphthalene, anthracene, and phenanthrene derivatives which have been produced during the year, mainly in connexion with the colour industry, and to which from want of space reference cannot be made, the following possess a certain theoretical interest :

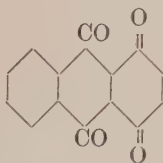
Atkinson and Thorpe¹ have succeeded in synthesising ethyl 1:3-diaminonaphthalene-2-carboxylate (II) by condensing ethyl sodio-cyanoacetate with benzyl cyanide, and treating the product (I) with strong sulphuric acid :



Orchardson and Weizmann² have prepared chloronaphthacene-quinone and certain other derivatives from hydroxynaphthoylbenzoic acid ;



And Dienel³ and Lagodzinski⁴ have independently obtained 1:4 anthraquinone, using the following method :



1:4-Anthraquinone.

α -Anthrol (I) is converted by nitrous acid into 2-(II) and 4-(III)

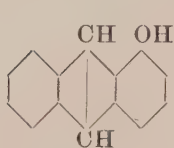
¹ *Proc.*, 1905, **21**, 305.

² *Trans.*, 1906, **89**, 115.

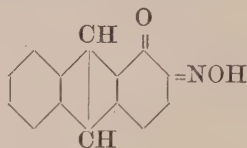
³ *Ber.*, 1906, **39**, 926.

⁴ *Ibid.*, 1717.

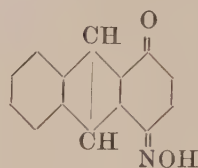
nitroso-1-anthrol, from which by reduction and subsequent oxidation 1:2- and 1:4-anthraquinone are formed :



I.

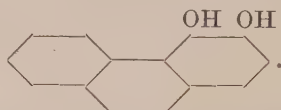


II.

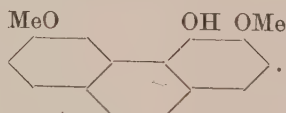


III.

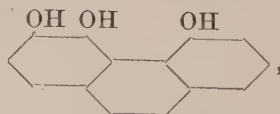
The important discovery by Vongerichten and Schrotter in 1881, that morphine when distilled over zinc dust yields phenanthrene, has given a definite direction to the study of derivatives of this hydrocarbon. Further investigation has shown that morphol—an integral part of the morphine molecule—is a dihydroxyphenanthrene :



The dimethyl ether of this phenol has since been synthesised by Pschorr and Sumuleanu.¹ Similarly, thebaine contains the complex 4-hydroxy-3:6-dimethoxyphenanthrene :



Morphenol, another morphine derivative, has now been converted by Vongerichten and Dittmer² into trihydroxyphenanthrene,

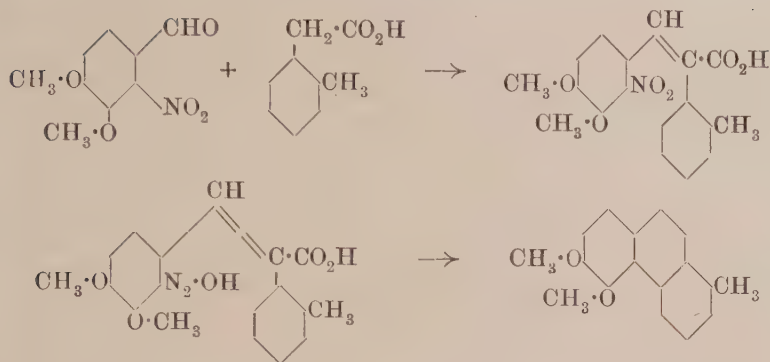


whilst Pschorr and his collaborators³ have succeeded in building up a series of hydroxyphenanthrene derivatives. The method is similar to that used in the preparation of 3:4-dimethoxyphenanthrene, of which the following single example must suffice. Condensation is effected between *o*-nitrovanillin methyl ether, sodium *o*-tolylacetate, and acetic anhydride. A nitrocinnamic acid derivative is obtained, which, on reduction and diazotisation, gives 3:4-dimethoxy-8-methylphenanthrene :

¹ *Ber.*, 1900, **33**, 1810.

² *Ibid.*, 1906, **39**, 1718.

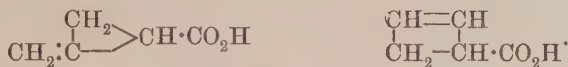
³ *Ibid.*, 3196,



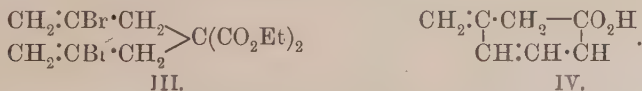
Hydrocyclic Compounds.

Sabatier and Mailhe¹ have successfully applied the well-known nickel reduction method² to the xlenols, and obtained the corresponding dimethylcyclohexanols.

Perkin, jun., in conjunction with Simonsen,³ has continued his researches on the synthesis of bridged rings. The action of sodium malonic ester on tribromopropane gives rise to a dibasic ester, $C_{12}H_{15}O_2Br$, which loses hydrogen bromide with potassium hydroxide. The product after hydrolysis loses carbon dioxide on heating and is transformed into a monobasic acid, to which the authors assign one of the following formulæ:



A second ester containing bromine, $C_{13}H_8O_4Br_2$, which is formed at the same time, is supposed to possess the constitution III, and loses hydrogen bromide with potassium hydroxide, yielding an acid which probably has the structure represented by IV:



A similar class of hydrocyclic compounds to those of formula IV have been studied by Wallach.⁴

The substances are obtained by condensing cyclic ketones with bromoacetic ester and zinc. The ester of the hydroxy-acid thus formed loses water when heated with potassium hydrogen sulphate, and passes into an unsaturated acid. The latter in turn loses carbon

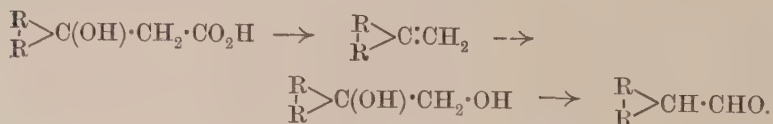
¹ *Compt. rend.*, 1906, **142**, 553.

² *Ann. Report*, 1904, 93.

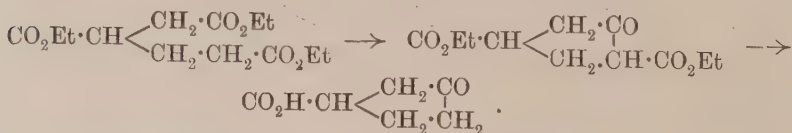
³ *Proc.*, 1905, **21**, 256; 1906, **22**, 133.

⁴ *Annalen*, 1906, **345**, 139; **347**, 316.

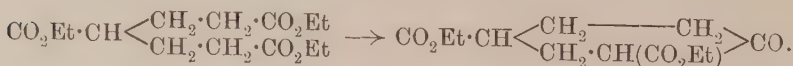
dioxide on heating and give methylene hydrocarbons, although the author does not commit himself to the view that the double-link is necessarily in the side-chain. These unsaturated hydrocarbons form nitrosochlorides and glycols in the usual way. The latter part with a molecule of water in presence of acids and give saturated aldehydes (see p. 130). The following scheme represents the changes which are supposed to occur:



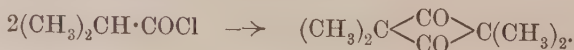
Perkin, jun., and Kay,¹ by condensing butane- $\alpha\beta\delta$ -tricarboxylic acid by heating with sodium, have obtained ethyl *cyclopentanone*-2:4-dicarboxylate and from it the monocarboxylic acid,



In a similar manner, ethyl pentane- $\alpha\gamma\epsilon$ -tricarboxylate yielded ethyl *cyclohexanone*-2:4-dicarboxylate:



Wedekind and Weisswange² have studied a new process for preparing diketones of the *cyclobutane* series by removing hydrogen chloride from acid chlorides with triethylamine. *iso*Butyryl chloride yields 1:3-diketotetramethyl*cyclobutane*,



Bauer and Breit³ have obtained *cyclobutane* derivatives from β -benzyl- β -styrylpropiophenone (from magnesium benzyl halide and cinnamylideneacetophenone, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} : \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$), and similar compounds by heating with equal parts of glacial acetic and sulphuric acids:



Grignard's reaction has also been utilised by Freundler⁴ for obtain-

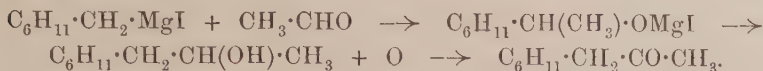
¹ *Trans.*, 1906, **89**, 1640.

² *Ber.*, 1906, **39**, 1631.

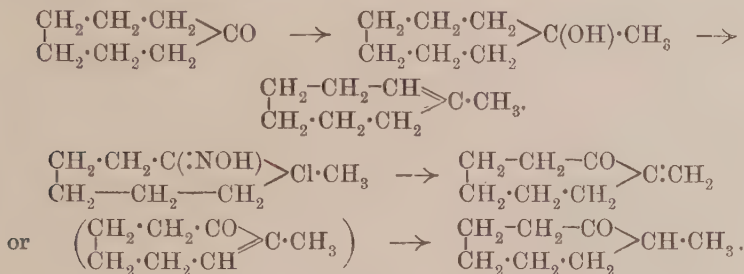
³ *Ibid.*, 1916.

⁴ *Compt. rend.*, 1906, **142**, 343.

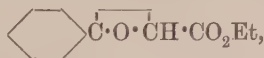
ing *cyclohexylacetone* from magnesium hexahydrobenzyl iodide and acetaldehyde :



Also by Wallach¹ for preparing methylsuberone and other heptacyclic derivatives. The stages of the process will be sufficiently indicated by the following formulæ :

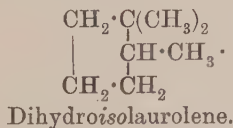


Aldehydes of *cyclohexane* have been obtained by Darzens and Lefébure by condensing *cyclohexanone* with monochloroacetic ester and sodium ethoxide. The glycid ester is easily hydrolysed, and the free



acid on distillation in a vacuum converted into hexahydrobenzaldehyde by loss of carbon dioxide.

The comparative study by Crossley and Renouf² of dihydro-laurole, dihydroisolaurole, and 1 : 1-dimethyl*cyclohexane*³ has led to the conclusion that dihydroisolaurole is 1 : 1 : 2-trimethyl*cyclopentane* and not a *cyclohexane* derivative, as proposed by Zelinsky and Lepeschkin, a conclusion which has been fully attested by Blanc's synthesis of *isolaurole* (p. 141).



In a series of interesting papers, Knoevenagel and others⁴ discuss the structure of two compounds obtained by Pinner⁵ and by Kerp and Müller⁶ by condensing acetone with itself, and termed *xylitones*. They appear to be derivatives of *cyclohexenone*, but although the authors have succeeded in synthesising a similar substance by condensing

¹ *Annalen*, 1906, **345**, 139.

² See *Ann. Report*, 1905, 120.

³ *Ibid.*, 1882, **15**, 586.

⁴ *Trans.*, 1906, **89**, 26.

⁵ *Ber.*, 1906, **39**, 3441 *et seq.*

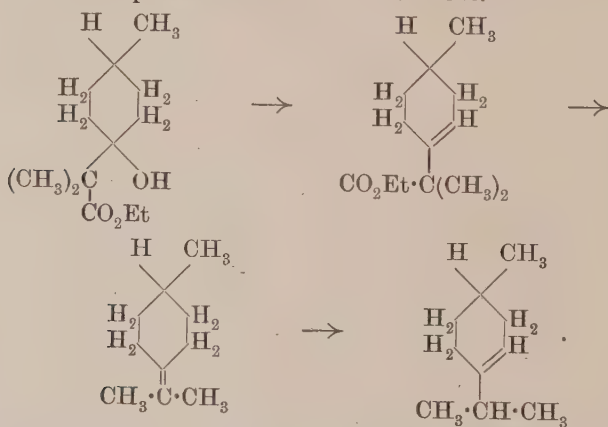
⁶ *Annalen*, 1898, **299**, 203.

phorone with ethyl acetoacetate, the constitution of the xylitones is still unknown.

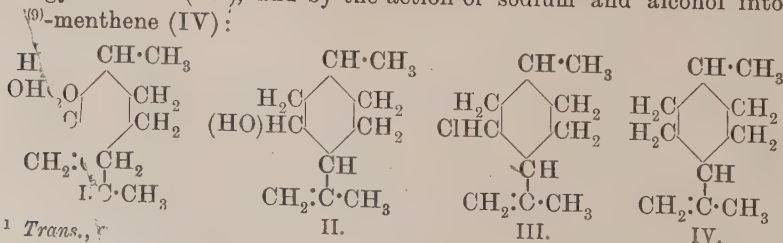
Terpenes and Camphors.

Among the synthetic preparations of members of the terpene and camphor group the following may be mentioned. Perkin, jun.,¹ has succeeded by methods previously described in obtaining tertiary menthol and Δ^3 -*p*-menthene from 1:4-methylcyclohexanone and magnesium isopropyl iodide. Kay and Perkin, jun.,² have also been successful in obtaining the active modification of Δ^3 -*p*-menthenol and $\Delta^{3:8(9)}$ -*p*-menthadiene by first resolving the 1-methyl- Δ^3 -cyclohexene-4-carboxylic acid into its enantiomorphs. The subsequent stages in the synthesis have already been described.³

A synthesis of menthene is also recorded by Wallach⁴ by condensing 1:4-methylcyclohexanone and ethyl α -bromoisobutyrate with zinc. The acid obtained from the product by hydrolysis loses carbon dioxide on heating and passes into *i*- $\Delta^{4(8)}$ -menthene, and on boiling the latter with sulphuric acid into *i*- Δ^3 -menthene.



A further synthesis of $\Delta^{8(9)}$ - and of active $\Delta^{3:8(9)}$ -menthadiene is described by Semmler and Rimpel.⁵ The starting point is α -citronellal (I), which is converted successively into isopulegole (II), *iso*- Δ^5 -ulegyl chloride (III), and by the action of sodium and alcohol into $\Delta^{8(9)}$ -menthene (IV):



¹ *Trans.*, 1906, 89, 832.

² *Ibid.*, 1906, 89, 832.

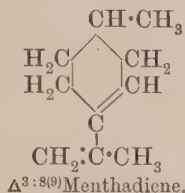
³ *Ibid.*, 1906, 89, 832.

⁴ *Ber.*, 1906, 39, 2504.

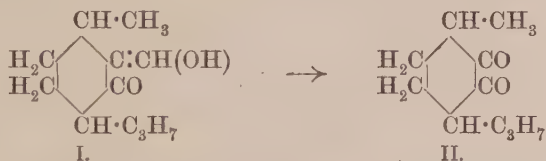
⁵ *Ann. Report*, 1905, 123.

⁶ *Ibid.*, 2582.

If *isopulegyl* chloride dissolved in quinoline is dropped into quinoline heated to 200—210°, it is transformed into $\Delta^3:8^{(9)}$ -menthadiene.

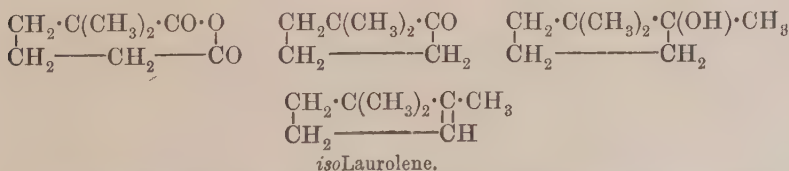


Semmler and McKenzie¹ have also succeeded in obtaining *Buchu-camphor* (found in the leaves of *Barosina betulina*) synthetically. It represents the enolic form of *p*-menthadione-2:3 (II). The synthesis was effected by the aid of hydroxymethylenementhone (I)², which is oxidised by means of ozone.



The diketone undergoes isomerisation under the influence of acids and alkalis to the enolic form, which is identical with the natural product.

Among other interesting syntheses is that of *isolaurolene* and *isolauronic* acid by Blanc,³ and *camphoric* acid by Perkin, jun., and Thorpe.⁴ Blanc's synthesis is effected by distilling *aa*-dimethyladipic anhydride under pressure, when it changes into dimethylcyclopentanone. The latter yields with magnesium methyl iodide and decomposition of the product a tertiary alcohol, which on distillation breaks up into water and *isolaurolene*:



The starting point for the new synthesis of *camphoric* acid is γ -bromotrimethylcyclopentanecarboxylic acid or its ester. The compound when shaken with a mixture of potassium cyanide and hydrogen cyanide and then heated gives an acid, which on boiling with acetic anhydride is

¹ *Ber.*, 1906, **39**, 1158.

² See *Ann. Chim. Phys.*, 1904, [viii], **3**, 49.

³ *Compt. rend.*, 1906, **142**, 1084.

⁴ *Trans.*, 1906, **89**, 795.

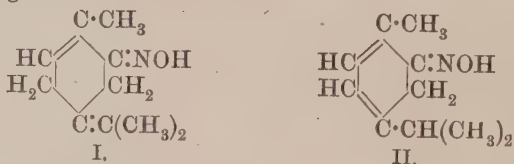
converted into *i*-camphoric anhydride, and from this camphoric acid can be prepared :



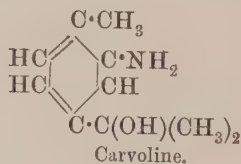
The numerous researches connected with the study of the structure of terpene and camphor derivatives can only be briefly indicated. Harries¹ finds by the ozone method that guttapercha contains the same fundamental hydrocarbon as Para rubber, namely, 1:5-dimethylcyclo-octa- $\Delta^{1:5}$ -diene, for it yields the same decomposition products.²

Wallach and Lautsch³ have made a study of the structure of *isocarvoxime*, which is formed when carvoxime hydrochloride or hydrobromide is treated with alcoholic potash.

As the substance is inactive, the choice of formulæ lies between the two following :



Further, *isocarvoxime* when heated with dilute sulphuric or oxalic acid is converted into a base *carvoline*. It is a hydroxycarvacrylamine,



and the mechanism of its formation from *isocarvoxime* (I) through (II) is fully discussed by the author.

In connexion with the terpenes, the study of nerol by v. Soden and Treff⁴ should be mentioned. The authors describe at length its method of separation, the preparation of numerous derivatives, and its behaviour with various reagents. Without discussing these in detail, it may be stated that the authors conclude, from the close similarity existing between geraniol and nerol, that the constitution of the two is very similar, and the association of nerol with linalool in essential oils points to an isomeric change in the latter under the influence of vegetable acids. They assign one of the following formulæ to the com-

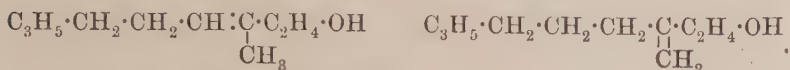
¹ Ber., 1905, **38**, 3985.

² Annalen, 1906, **346**, 266.

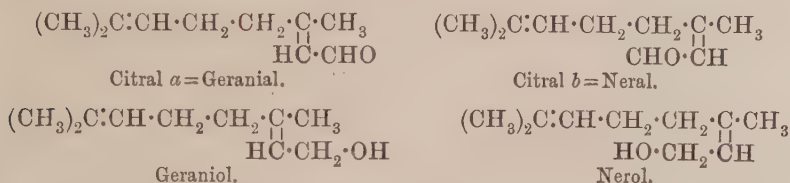
³ Ann. Report, 1905, 126.

⁴ Ber., 1906, **39**, 906.

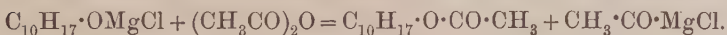
pound, but give preference to the second, in which the central double bond of geraniol is displaced :



In another paper by Zeitschel¹ on the same subject, the author comes to the conclusion that geraniol is stereoisomeric with nerol. He shows that by the action of acetic anhydride and other reagents linalool can be converted not only into geraniol and terpineol, but into nerol, by a process of isomeric change. The two stereoisomerides are further shown to be directly connected with the isomeric citrals *a* and *b*, which are likewise stereoisomeric :



The conversion of pinene hydrochloride into borneol and bornyl acetate has been effected by Houben² by means of magnesium. Magnesium pinyl chloride, which is formed, is exposed to a current of oxygen and then decomposed with sulphuric acid or acetic anhydride. In the former case borneol, in the latter the acetate, is formed :



Tilden and Shephard³ find that magnesium methyl iodide converts α - and β -limonene nitrosochloride into isomeric compounds of the formula $\text{C}_{20}\text{H}_{32}\text{ON}_2\text{Cl}_2$ by removing oxygen from the bisnitrosochloride.

Rupe and Liechtenhan⁴ have obtained from carvone by means of magnesium methyl iodide a hydrocarbon, $\text{C}_{11}\text{H}_{16}$, and a small quantity of a ketone, $\text{C}_{11}\text{H}_{18}\text{O}$, of unknown constitution. A long and important paper on derivatives of pinene by Wallach⁵ does not admit of useful abstraction, and the reader must be referred to the original memoir.

Colour and Structure.

In the two former *Reports* an indication was given of the direction of research on the relation of colour to structure, and a brief reference was also made to the results which might be anticipated from the work of Hartley and others on absorption spectra. During the past year

¹ *Ber.*, 1906, **39**, 1780.

² *Ibid.*, 1700.

³ *Trans.*, 1906, **89**, 920.

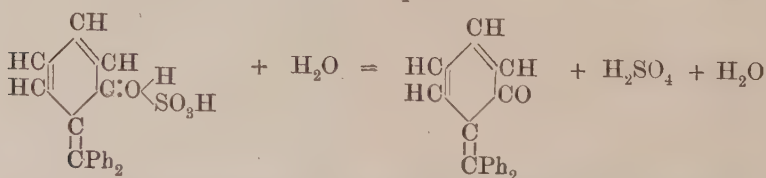
⁴ *Ber.*, 1906, **39**, 1119.

⁵ *Annalen*, 1906, **346**, 220.

the subject has been actively pursued, and many of the views formerly advanced have been modified, matured, or moulded into definite shape.

The absorption bands in the ultraviolet portion of the spectrum of a large number of coloured and colourless compounds have been submitted by Hartley and his collaborators to careful examination and measurement, and have led him to the following views on the structure of coloured substances. The formation of a colouring matter from a benzene derivative depends on the introduction of such modifications of the structure of the molecule as will displace the absorption bands towards the visible portion of the spectrum; that is, by retarding the rate of oscillation. But whilst the colour depends on the peculiar kind of oscillation of the benzene ring, the retardation may be effected by replacing hydrogen by hydroxyl or amino-groups (Witt's auxochromes) or by the condensation of several benzene nuclei. Thus, the condensation of three benzene nuclei into triphenylmethane is manifested by the decrease in number of oscillations and increase in their intensity, whereby the bands are displaced to the edge of the visible spectrum. The characteristic six bands of benzene become fused into a broad band on the fringe of the ultraviolet. These views have been accepted by v. Baeyer, for they appear to harmonise with his latest investigation on the relation of colour to structure.¹

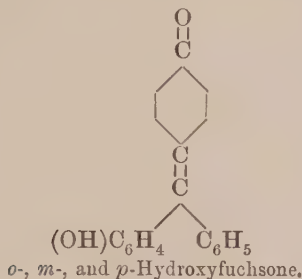
The coloured solutions of *o*-trianisylcarbinol and *o*-hydroxytriphenylcarbinol in acetosulphuric acid are no longer ascribed to the union of the acid with the quinone oxygen which becomes quadrivalent, for the decomposition of the salt by water should give at least a passing indication of the formation of the coloured quinone:



But this only occurs where there is a hydroxyl already in the para position to the carbinol group. It therefore follows that the colour of triphenylcarbinol salts is not necessarily connected with the quinone structure of its hydroxy- or halogen derivatives. v. Baeyer consequently returns to his original view, according to which the cause of colour is due to the multiplication of benzene nuclei in triphenylcarbinol. The chromophore includes the whole complex which already possesses the power of manifesting colour, and only requires a chemical change such as that produced by union with sulphuric acid to make it evident. In the language of Witt, triphenylmethane is the chromophore and the

¹ *Zeit. angew. Chem.*, 1906, **29**, 1287.

sulphate group, the auxochrome. The author has prepared various hydroxy-derivatives of fuchsone which dissolve in alkalis with characteristic colours, para with violet, ortho with blue, and meta with blood-red. To these compounds, which may be regarded as anhydrides of a *p*-hydroxycarbinol, the following quinonoid structure is given :

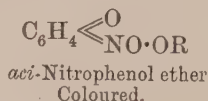
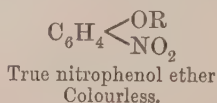


If excess of alkali is added the colour vanishes, and this is explained by the addition of the elements of water and the formation of a hydroxycarbinol. The addition of acid reproduces the colour, but at a rate varying with the position of the hydroxyl group. The *p*-hydroxyfuchsone is precipitated at once as the yellow quinone, whereas the *o*- and *m*-compounds separate as colourless carbinols, and only slowly lose water and pass into the quinonoid form.

Thus, the hydroxytriphenylcarbinols possess in a varying degree the basic properties of an alkali, and like the latter lose water on union with acids. The same views hold in regard to the amino-derivatives, but in this case it is necessary for colour to be manifested, that not one but the two amino-groups should occupy a para position to the central carbon atom. Why this is necessary is not explained, but the fact remains that with only one quinonoid amino-group the compound is colourless; but here again many of the salts are coloured. In a former *Report*¹ a brief outline was given of Hantzsch's views on the relation between colour and constitution. He assumed that the change from a colourless to a coloured substance generally denotes a concurrent change of structure. This principle has now been applied to the nitrophenols. All true nitrohydrocarbons are colourless; so are the structurally immobile derivatives of nitrophenols like the ethers and esters. Thus, the nitro-group itself is destitute of chromophoric properties. On the other hand, certain nitrophenols and all their salts are coloured. This has been usually explained by saying that the chromophoric character of the nitro-group is enhanced by the auxochromic hydroxyl. The view is contested by Hantzsch, who brings evidence to show that there exist two series of ethers, namely, colour-

¹ *Ann. Report*, 1904, 122.

less or true nitrophenol ethers, and coloured quinonoid or *aci*-nitrophenol ethers. They are represented by the general formulæ :



Every case of colour in the nitrophenol group is explained in the light of these new facts. Thus, the free nitrophenols which are coloured consist of a solid solution or equilibrium mixture of the two dynamic isomerides, the colour intensity depending on the proportion of the coloured or *aci*-constituent present. Picric acid is a case in point. The alkali salts represent the preponderating *aci*-form. One fact requires explanation. The salts of picric acid are much lighter in colour than the *aci*-picric ethers which have a red colour. The explanation is that there are two series of *aci*-ethers, a light and a dark coloured one. The picrates correspond to the light coloured series. The change of colour is not only effected by conversion of the nitrophenols into their salts, but by rise of temperature and by solvents. Light petroleum produces a colourless solution, whereas water, with its greater ionising power, produces a certain amount of the coloured *aci*-structure. Hantzsch, however, does not subscribe to the view that ionisation alone produces colour, because the ions of acids which give rise to coloured salts may exist without colour. The existence of coloured and colourless nitrophenol ethers which are non-ionisable compounds is sufficient evidence of the fact. The colour change is essentially a structural or chemical change in the first instance, and ionisation is only a secondary phenomenon. Thus the idea of chromophore and auxochrome as separate and distinct factors in colour production does not hold, but the phenomenon of colour is the effect of a chemical interchange which is promoted by their association in the same compound :



Both forms possess a dissociation constant in aqueous solution, but at present there appears no way of determining it. The fact that the alkali salts as well as the free nitrophenols deepen in colour on heating when the *aci*-form is almost wholly present is ascribed to a changing proportion of the yellow variety, or to a greater or less dissociation of the *aci*-compound. *o*-, *m*-, and *p*-Nitrophenols give coloured salts, and therefore possess a quinonoid structure, although no *m*-quinonoid ethers have so far been prepared.

The many apparently contradictory facts have been so ingeniously met by Hantzsch that the theory almost disarms criticism. Not-

withstanding, Kauffmann¹ has taken up the defence of the auxochrome theory, and bases it, in the first place, on the change in the position of the absorption band produced in benzene by the introduction of different groups; in the second place, on the existence of coloured nitroethers like nitroquinol dimethyl ether, and nitrohydrocarbons like nitrostilbene. The existence of Hantzsch's colourless ether is ascribed by Kauffmann, to the weak auxochromic character of the acetyl and methoxyl groups. Hantzsch in reply points out that the absorption spectra cannot determine the presence or absence of auxochromic groups, because no relation has been shown to exist between them; he throws doubt on the purity of the coloured specimen of nitroquinol dimethyl ether, and lays aside the question of the general structure of coloured substances as outside the present discussion, which only embraces those compounds which exhibit a simple change from colourless to coloured.

In reference to absorption bands, he supports his contention by Baly's observation² of the similarity of the bands of colourless *p*-nitrophenol and its methyl ether, and the great divergence exhibited by the coloured sodium salt.

In a further paper³ Hantzsch brings evidence to show that the colour of the salts of colourless phenol aldehydes and their ethers must be ascribed to a similar structural change,



and the same explanation has been applied to the case of the hydroxy-ketones and hydroxybenzoic acids.

A similar principle to that of Hantzsch has been adopted by Green and King⁴ in support of their view of the quinonoid structure of the phthaleins. They bring evidence to prove the existence of coloured quinonoid alkyl esters of the phthaleins such as



and hence regard the coloured salts of these compounds as possessing an analogous structure, the sodium salt having the formula,



The relation of colour to structure is viewed by Baly and his collaborators from a very different standpoint. Hantzsch's explanation of colour phenomena is, in a sense, a statical one, depending on a particular structure, which, however, is not necessarily opposed to the views of Hartley, Baly, or v. Baeyer. Baly's view is essentially dynamical. The absorption spectra in the ultra-violet of certain coloured and colourless substances show characteristic bands which are

¹ *Ber.*, 1906, **39**, 1959.

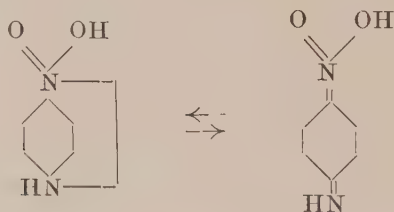
² *Trans.*, 1906, **89**, 518.

³ *Ber.*, 1906, **39**, 3080.

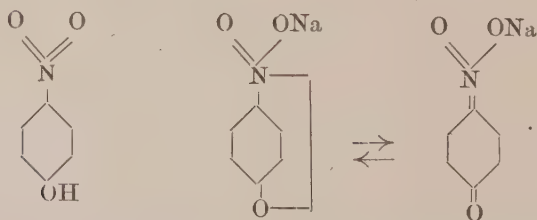
⁴ *Ibid.*, 2365.

ascribed by Baly to the presence of mobile groups (usually associated with dynamic isomerism) which give to the molecule, by virtue of their *potential tautomerism*, a rapid vibration or oscillation termed *isorro-pesis*. The theory embraces a variety of diverse phenomena such as tautomerism, steric hindrance, structure, and colour. Thus, the tautomerism of acetoacetic ester¹ and similar substances is supposed to be manifested by distinctive ultra-violet absorption bands which they exhibit in solution.

The reactivity of the α -diketones and quinones is associated with other prominent absorption bands,² and the colour of some of the members of these groups is traced to internal oscillations set up by change of structure in the ketone groups. This change of structure is ascribed to the change of residual affinities of the ketone oxygen atoms. The quinonoid structure is regarded as the statical representation of such an internal oscillation which affects the visible region of the spectrum. The colour of the nitroanilines and nitrophenols³ is ascribed in the same way to oscillations set up by the change of the residual affinities of the nitrogen and oxygen and the two nitrogen atoms respectively :



p-Nitrophenol in alcoholic solution and its sodium salt are represented by :



The free phenol is statical and colourless, the sodium salt dynamical and coloured.

The same principle has been applied to determining the structure of the *isonitroso*-compounds which are colourless in the free state and

¹ *Trans.*, 1904, **85**, 1039.

² Baly and Stewart, *Trans.*, 1906, **89**, 489, 502.

³ Baly, Edwards, and Stewart, *Trans.*, 1906, **89**, 514.

coloured in alkaline solution.¹ Finally, the diminished persistence of the absorption bands in the case of the substituted quinones is advanced to explain the diminished reactivity of the quinone group formerly attributed by Kehrmann to steric influences.²

In summing up the theories of the four chemists whose work has been described, it will be seen that those of Hartley and Baly are essentially dynamical. Colour is manifested by molecular vibration; but whilst Hartley is satisfied with formulating the principle that a particular molecular structure gives rise to bands which by displacement may become visible as colour, Baly goes further, and postulates a potential change of structure as being responsible for the oscillations which are set up, thus manifesting in certain cases the phenomenon of colour. v. Baeyer and Hantzsch confine their attention to structure, without discussing specifically the nature of those molecular oscillations which must be in every case its ultimate cause. Whilst Hantzsch limits his investigation to those compounds which change readily from a colourless to a coloured modification, and explains the process by a definite isomeric change, Baeyer attacks the broader question of structure and colour, and finds the answer in Hartley's theory, which has already been discussed.

J. B. COHEN.

¹ Baly, Marsden, and Stewart, *Trans.*, 1906, **89**, 966.

² Stewart and Baly, *Trans.*, 1906, **89**, 618.

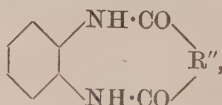
ORGANIC CHEMISTRY—HETEROCYCLIC DIVISION.

The work of the past year among heterocyclic compounds exhibits the usual variety ; from a theoretical point of view, the chief interest attaches to the questions of ring-formation and the salt-forming properties of numerous substances which contain oxygen or sulphur as members of a ring.

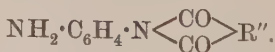
Whilst there are no startling results to record in the uric acid group or amongst the naturally occurring organic dyestuffs, two alkaloid groups (the quinine and morphine groups) have received a great deal of attention.

Ring-formation.

A matter which receives constant attention is that of the number of members possible in a closed-chain compound. A second communication by R. Meyer ¹ contains an account of the results obtained on condensing dibasic acids with the isomeric diaminobenzenes. *o*-Phenylenediamine normally condenses to give compounds of the general type



where R'' may be as large as C_8H_{16} , *o*-phenylenesebacamide having been isolated. Similar closed-ring amides cannot be produced from *m*- and *p*-phenylenediamines ; the compounds obtained are certainly isomeric, but contain a free amino-group, and have to be formulated thus :

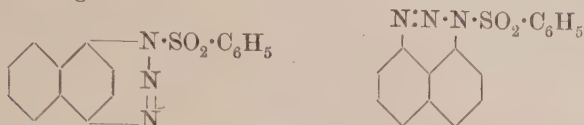


On the other hand, G. T. Morgan and F. M. G. Micklethwait ² are inclined to assume the existence of *para*-bridged rings in the case of the diazoimides obtained by the action of nitrous acid on monoaryl-sulphonyl-*p*-diamines. These have been occasionally formulated with a quinonoid structure, but the products obtained from the benzene-sulphonyl derivatives of 1 : 4- and 1 : 8-naphthylenediamines show such great similarity as to render any difference in structure very im-

¹ *Annalen*, 1906, **347**, 17.

² *Trans.*, 1906, **89**, 4, 1158 ; and *Ber.*, 1906, **39**, 2869.

probable. The *peri*-compound cannot possess a quinonoid constitution, and consequently the authors formulate the 1:4- and 1:8-derivatives in the following manner :

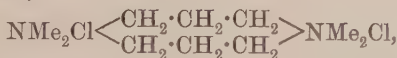


It may be noted that a similar ring structure is assigned by W. Vaubel and O. Scheuer to the diazoamine resulting from the action of nitrous acid on benzidine.¹ This substance reacts with hydrochloric acid to yield 4-aminodiphenyl-4'-diazonium chloride.

Several compounds containing eight-membered rings have been described during the past year ; thus *o*-phenylenediamine and succinaldehyde condense readily, forming a substance which has a normal molecular weight. On this account, C. Harries and H. Krützfeld assign to the substance the following constitutional formula :²



Another case in which an eight-membered ring is easily produced is seen in L. Knorr's and P. Roth's study of the spontaneous polymerisation of dimethyl- γ -chloropropylamine.³ The resulting *di*-quaternary ammonium chloride,



yields *iso*allyl ether, dimethylallylamine and tetramethyltrimethylene-diamine on distillation with potash. These results induced H. Ilörlein and R. Kneisel⁴ to examine further the quaternary salt obtained by Gabriel and Stelzner⁵ from 1- γ -bromopropylpiperidine ; in this case a similar conclusion is arrived at, namely, that two molecules condense, with formation of an eight-membered ring.

On the other hand, J. von Braun⁶ finds that the double formula he suggested for bis-piperidonium bromide is incorrect, and that the substance must be represented as



The substance is only attacked with difficulty by ammonia, and then a compound,



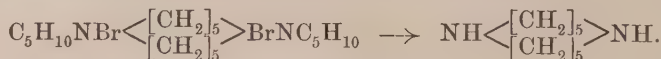
¹ *Zeit. Farb. Text. Ind.*, 1906, **5**, 61.

² *Ber.*, 1906, **39**, 3670.

³ *Ber.*, 1906, **39**, 1420 ; compare S. Gabriel and J. Colman, *Ber.*, 1906, **39**, 2875.

⁴ *Ber.*, 1906, **39**, 1429. ⁵ *Ibid.*, 1896, **29**, 2389. ⁶ *Ibid.*, 1906, **39**, 4347.

results, whilst had the double formula been correct, another compound with a twelve-membered ring should have been formed,



J. von Braun and C. Müller¹ also find that the production of the eight-membered ring—heptamethyleneimine—by heating heptamethylenediamine is impossible; only a polymeride has been isolated in the form of its platinichloride.

E. E. Blaise and Houillon² find that a base of the composition $\text{C}_8\text{H}_{17}\text{N}$ results by the elimination of a molecule of ammonia from octamethylenediamine, but instead of containing a nine-membered ring, it is identical with 2-butylpyrrolidine which they have synthesised for purposes of comparison from β -butyrylpropionic acid. More recently they have shown³ that the supposed decamethyleneimine of Krafft and Phookan⁴ is in reality 2-hexylpyrrolidine.

Relationship between Structure and Basicity.

During the past year several papers have appeared devoting attention to the relationship existing between the structure of cyclic compounds and their strength as bases. G. Dedichen⁵ finds that glyoxaline is a much stronger base than the isomeric pyrazole, the respective affinity constants being 1.2×10^{-7} and 3.0×10^{-12} . The substitution of methyl for hydrogen increases the basicity in the glyoxaline series, and also in the pyrazole series if it is hydrogen atoms attached to carbon that are substituted; on the other hand, the basicity is diminished by substitution with regard to the imino-group. Both the triazoles and the isodihydrotetrazines are found to be very weak bases, an increase in strength again being observed when hydrogen attached to carbon is replaced by methyl.

G. T. Morgan and F. M. G. Mickelthwait⁶ find that coumarin is slightly basic, and forms salts of abnormal type such as



6-Aminocoumarin, however, gives salts of normal composition (for example, $2\text{C}_9\text{H}_5(\text{NH}_2)\text{O}_2 \cdot \text{H}_2\text{PtCl}_6$, but when the amino-group is acetylated, the salts produced are again of the same type as those furnished by coumarin itself. The paper contains a discussion on the subject of residual affinity, and the same subject has attracted A. Hantzsch and O. Denstorff,⁷ who have prepared many addition products of halogens and per-halogen hydracids with oxygen

¹ *Ber.*, 1906, **39**, 4110.

² *Ibid.*, 1906, **143**, 361.

³ *Ber.*, 1892, **25**, 2252; see also Krafft, *Ber.*, 1906, **39**, 2193.

⁴ *Ber.*, 1906, **39**, 1831. ⁵ *Trans.*, 1906, **89**, 863. ⁶ *Annalen*, 1906, **349**, 1.

⁷ *Compt. rend.*, 1906, **142**, 1541.

compounds. The fact that dimethylpyrone frequently forms salts in which two molecules of the basic oxygen compound are united to one molecule of the acid, for example, $(C_7H_5O_2)_2HBr_3$, raises the question as to whether the oxygen really becomes quadrivalent, or if the halogen or per-halogen acid is not rather attached by a "Nebenvaleanz."

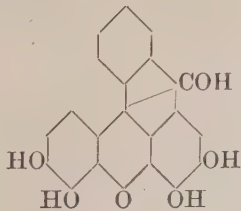
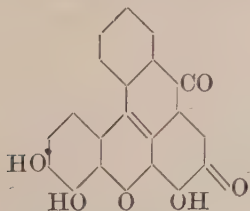
But although ethers do not take up alkyl iodides with the readiness exhibited by most tertiary amines, the two classes of compounds show a certain similarity in their behaviour towards dimethyl sulphate. F. Kehrmann and A. Duttenhöfer¹ found that this ester and dimethylpyrone slowly combine; after four weeks at the ordinary temperature, and a further eight days with a small addition of dimethyl sulphate, the mass, on solution in water and addition of potassium iodide, yields a tertiary oxonium iodide which the authors think is most probably represented by the formula $CO \begin{smallmatrix} \text{CH:CMe} \\ \text{CH:CMe} \end{smallmatrix} O \begin{smallmatrix} \text{Me} \\ \text{I} \end{smallmatrix}$.

Further examples of the residual affinity of furan, pyrrole, and thiophen derivatives are afforded by the work of K. A. Hofmann and H. Arnoldi,² and F. Wager and B. Tollens.³

The similarity of functions exercised by oxygen, sulphur and the imino-group is exemplified in the coeroxene, coerthiene and coeramidene compounds examined by H. Decker and his co-workers.⁴ These three substances



derive their name from coerulein, a colouring matter prepared by A. von Baeyer by the action of sulphuric acid on pyrogallolphthalein.⁵ The constitutions of this colouring matter and its leuco-compound were eventually shown by Orndorff and Brewer⁶ to be



¹ *Ber.*, 1906, **39**, 1299.

² *Ibid.*, 339.

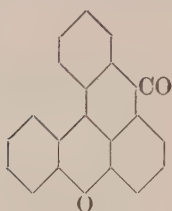
³ *Ibid.*, 410.

⁴ *Annalen*, 1906, **348**, 210.

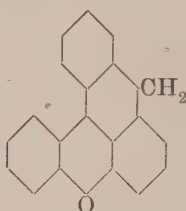
⁵ *Ber.*, 1871, **4**, 555, 658.

⁶ *Amer. Chem. J.*, 1906, **23**, 425; 1901, **26**, 96.

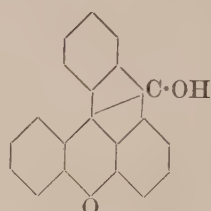
respectively. These substances, in the nomenclature employed by Decker, are trihydroxycoeroxenone and tetrahydroxycoeroxenol, whilst for other important compounds containing the same nucleus the following names are proposed :



Coeroxone-9.

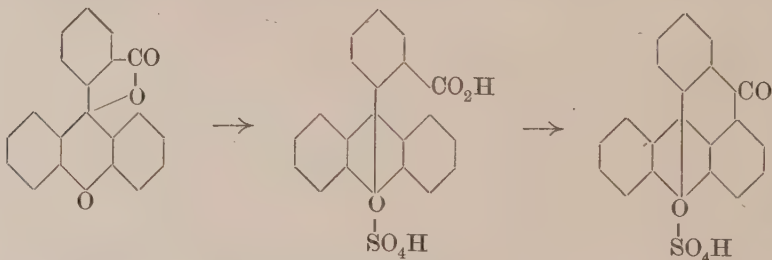


Coeroxan.

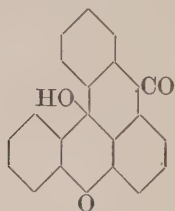


Coeroxenol-9.

The coeroxonium salts are obtained by the action of fuming sulphuric acid on fluoran and its derivatives. The latter first dissolve with the formation of yellow salts ; water is then eliminated and red coeroxonium salts are produced.



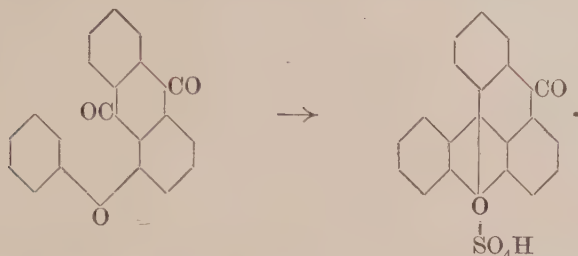
The superior stability of the coeroxonium salts as compared with those of fluoran furnishes a ready method of separation. The coeroxonium salts correspond to a carbinol *pseudo*-base, ethers of which may be prepared as in the acridanol series ; these compounds are formulated in the following manner :



Coeroxenol, the reduction product of the coeroxonium salts, is scarcely capable of isolation, but if the reduction is carried out in presence of acetic anhydride, its acetyl derivative is obtained. Employment of hydriodic acid and phosphorus as reducing agents or distillation with zinc dust give coeroxene.

A quite independent method of synthesising coeroxonium salts has

been worked out by H. Decker and E. Laube;¹ this consists in the condensation of 1-phenoxyanthraquinone with concentrated sulphuric acid:

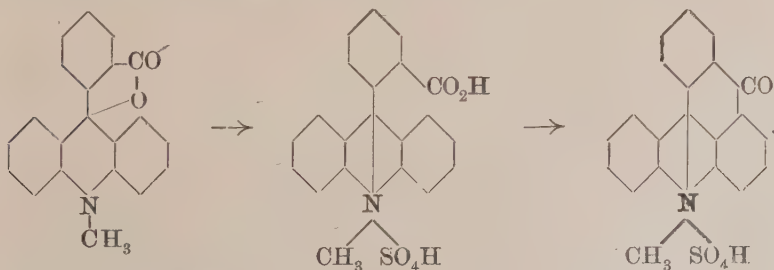


Laube has prepared similar derivatives of the naphthalene series by employing the α - and β -naphthyl ethers of erythroxyanthraquinone.²

The sulphur analogues of these compounds have been prepared by H. Decker and A. Würsch³ by the condensation of 1-phenylthioanthraquinone with sulphuric acid, whilst the substance for which Decker proposes the name coeramidonine was first prepared by the Farbenfabriken vorm. F. Bayer⁴ from α -anilinoanthraquinone, and shown to possess the structure



by R. Dannemann and L. Gattermann.⁵ Decker and C. Schenk⁶ find that it is most readily prepared by the condensation of acridylbenzoic acid with a mixture of concentrated and fuming sulphuric acid; the base gives quaternary ammonium salts which may also be obtained by the action of sulphuric acid on the lactone of 5-hydroxy-5-phenyl-10-methyldihydro acridinecarboxylic acid:



¹ *Annalen*, 1906, **348**, 231.

³ *Annalen*, 1906, **348**, 238.

⁵ *Zeit. Farb. Text. Ind.*, 1902, **1**, 325.

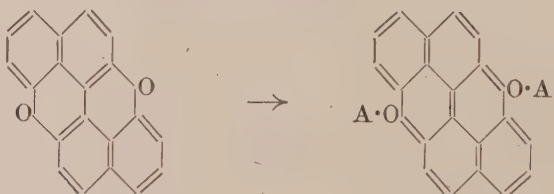
² *Ber.*, 1906, **39**, 2245.

⁴ D.R.-P. 120193.

⁶ *Annalen*, 1906, **348**, 242.

The last reaction, it will be noted, is the exact analogue of the formation of coeroxonium salts from fluoran.

Somewhat similar relationships to those holding between coeroxene and the coeroxonium salts have been observed in the case of dinaphthylene dioxide.¹ Decker finds that this substance dissolves in concentrated sulphuric acid with a bright yellow colour and violet fluorescence, but on adding an oxidising agent the colour changes to blue from the production of an oxonium salt :



Pseudo-Bases.

The relationship of quaternary ammonium salts to *pseudo*-bases has again attracted a considerable amount of attention, and the views advocated by Hantzsch and by Decker with regard to acridine derivatives have received striking confirmation through C. K. Tinkler's study of the absorption spectra of several acridine derivatives.²

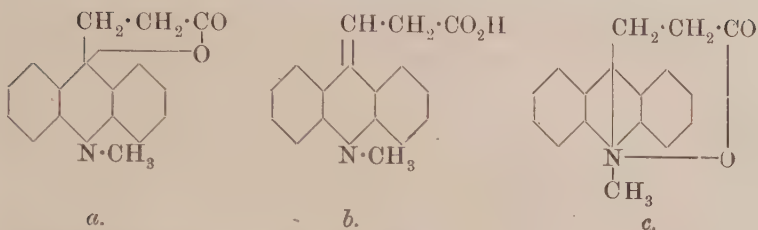
Acridine methiodide and acridine hydrochloride give practically identical absorption spectra, but when caustic soda is added to an aqueous alcoholic solution of the methiodide, the absorption spectrum assumes a close resemblance to that of dihydroacridine. Similar changes have been observed with the methylacridine derivatives, and analogously phenanthridine methiodide and the corresponding hydroxide give quite different absorption spectra, the spectrum of the latter resembling that of Pictet and Ankersmit's dihydrophenanthridine. Tinkler further shows that the cyanides obtained from the methiodides are not true salts, but rather *pseudo*-cyanides ; their absorption spectra are almost identical with those of the dihydroacridines and of the *pseudo*-bases.

A very interesting question relating to *pseudo*-bases in the acridine series has been examined by C. Schenk.³ Suppose acridylpropionic acid to be converted into its methyl ester and this in turn into a methiodide. By the action of alkali, the methyl attached to carboxyl will be hydrolysed, and the elements of hydriodic acid will be removed. The resulting base may be expected to be (a) a lactone, (b) an unsaturated acid, or (c) a betaine, as shown by the formulæ :

¹ *Ber.*, 1906, **39**, 3069.

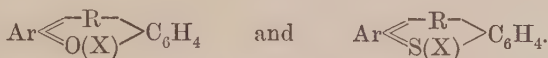
² *Trans.*, 1906, **89**, 856.

³ *Ber.*, 1906, **39**, 2424.



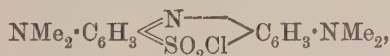
The experimental result showed that a colourless lactone is precipitated from the solution, but this dissolves in water to a certain extent as a betaine salt exhibiting a yellow colour and strong fluorescence. By the addition of hydrochloric acid to this solution, acridylpropionic acid methochloride is produced.

The question of the constitution of the oxazine and thiazine dyes has received much attention from Hantzsch and Kehrman.¹ Hantzsch considers these dyes to possess a *para*quinonoid structure and to be quaternary ammonium salts. Kehrman, on the other hand, considers them to be *ortho*quinonoid oxonium or thionium salts; against the latter view, Hantzsch² brings forward the fact that salts of the types



(Ar = bivalent aromatic radicle, R = N, X = acid radicle), which Kehrman regards as the parent substances of Meldola's blue and methylene-blue, are the salts of very weak bases and entirely hydrolysed by an excess of water. Meldola's blue and methylene-blue are, on the contrary, quite stable salts, and this difference cannot be explained simply by the substitution of amino-groups for hydrogen, for, taking a simple case, *o*-phenylenediamine is actually a weaker base than aniline.

A further argument of Hantzsch's is not so happy; Bernthsen obtained a substance, methylene-azure,³ by the oxidation of methylene-blue, and in this he supposed the sulphur had been oxidised to a sulphone group. Hantzsch, accepting this view, states that according to Kehrman, the chloride of methylene-azure must have the structure



which would accord better for behaviour with an acid chloride than with a salt. This argument is, however, quite valueless, since Kehrman has shown that methylene-azure does not contain oxygen, and

¹ See *Ann. Report*, 1905, 139.

² *Ber.*, 1906, 39, 153.

³ *Annalen*, 1885, 230, 169.

further that it results from methylene-blue by removal of one or more methyl groups;¹ this result is fully confirmed by Bernthsen.²

Kehrmann has further compared the properties of a number of substances in the methylene-blue series.³ Adopting his nomenclature, these are the chlorides of: (I) dimethylphenazthionium; (II) anilino-phenazthionium; (III) acetylaminophenazthionium; (IV) amino-phenazthionium; (V) diacetylthionine; (VI) thionine, and (VII) methylene-blue. Of these chlorides, none, according to Kehrmann, is totally hydrolysed in solution; I and II are partially hydrolysed, III and IV somewhat less, and V, VI, and VII not at all.

Hantzsch⁴ cannot see that these results in any way nullify his argument; all they do is to render Kehrmann's theory more improbable. To take an extreme case, even supposing a thionium salt of the stability of methylene-blue could be prepared, it would not then be proved that methylene-blue was necessarily a thionium salt, but merely that it might equally as well possess a thionium as an ammonium constitution.

Another question which has received considerable attention in the last few years is respecting the constitution of aposafranone and allied compounds. From the inability of *isorosindone* to react with magnesium phenyl halides, H. Decker and A. Würsch⁵ conclude that the internal ammonium phenoxide formula is the more probable.

Syntheses.

A number of new compounds containing well-known heterocyclic groupings have been prepared during the past year.

Pyrrole Group.

C. Bülow and C. Sautermeister have further examined the *N*-amino-pyrrole derivative obtained by condensing hydrazine hydrate with ethyl diacetylsuccinate; the amino-group reacts with phenylthiocarbimide to give a thiocarbamide derivative,⁶ and Bülow with R. Weidlich⁷ finds that it is possible to bring both amino-groups into reaction with ethyl diacetylsuccinate if symmetrical dihydrazides such as malonylhydrazide, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$, are employed.

N-Substituted pyrroles from ethyl diacetylsuccinate and phenetidine are described by L. Rossi,⁸ whilst the condensation of 1:4-diketones with ammonia has been the subject of a study by W. Borsche and A. Fels.⁹ The change actually takes place in two stages, an un-

¹ *Ber.*, 1906, **39**, 1403.

² *Ibid.*, 1804.

³ *Ibid.*, 914.

⁴ *Ibid.*, 1365.

⁵ *Ibid.*, 2653.

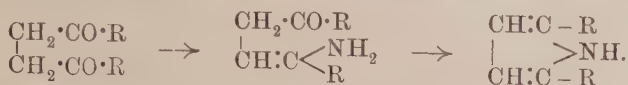
⁶ *Ibid.*, 647.

⁷ *Ibid.*, 3372.

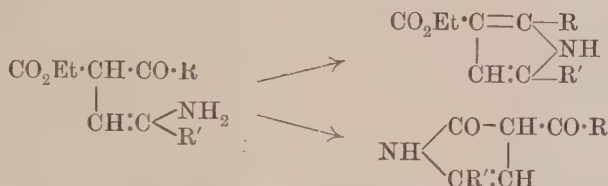
⁸ *Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 299.

⁹ *Ber.*, 1906, **39**, 3877.

saturated amino-ketone being first produced; this then undergoes a further condensation:

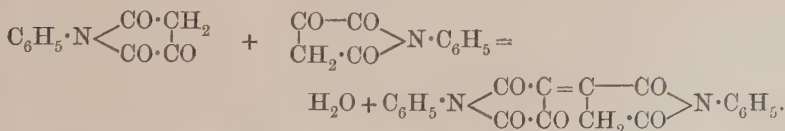


The only case hitherto known of the isolation of such an intermediate product is the ethyl β -amino- Δ^8 -hexene-3-one- $\gamma\delta$ -dicarboxylate obtained by Knorr and Rabe¹ from ammonia and ethyl diacetyl-succinate. The present authors increase the number of observed cases, and have obtained unsaturated amino-ketones from ethyl phenacylacetoacetate and ethyl acetylbenzoylacetoacetate; the structure of the compounds is rendered quite certain by the possibility of transforming them not only into pyrrole derivatives but also into keto-lactams.



The hydrogenation of pyrrole to pyrrolidine, using reduced nickel at 180–190° as catalyst, has been studied by M. Padoa;² and the opening of the pyrrolidine ring by benzoylation and subsequent treatment with phosphorus pentachloride or pentabromide has been examined by J. von Braun and E. Beschke.³ According to the temperature at which the reaction is carried out benzoylpyrrolidine may be made to yield either benzo- δ -chlorobutylamide or $\alpha\delta$ -dichlorobutane.

S. Ruhemann⁴ shows that the substances obtained by Wislicenus and Sattler⁵ by the action of sodium ethoxide on mixtures of ethyl oxalate and the acetyl derivatives of primary aromatic amines contain rings made up of one nitrogen and four carbon atoms. The so-called xanthoxalanil results from an indogenide condensation of the first-formed product in the following manner:



Hæmopyrrole has received considerable attention from W. Küster,⁶

¹ *Ber.*, 1900, **33**, 3801.

² *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 219.

³ *Ber.*, 1906, **39**, 4119.

⁴ *Trans.*, 1906, **89**, 1236, 1847.

⁵ *Ber.*, 1891, **24**, 1245.

⁶ *Annalen*, 1906, **346**, 1.

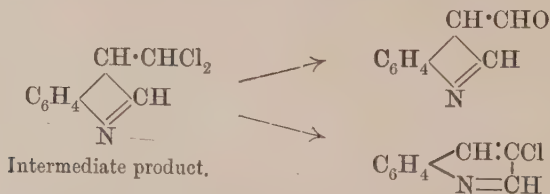
and R. Willstätter describes the substances isolated from the first steps in the hydrolysis of chlorophyll;¹ the interest of both these papers is largely physiological.

Indole and Indigo.

A few new indole derivatives have been prepared. D. J. Grgin obtains 3:3:5-trimethylindolenine by the reaction between *p*-tolylhydrazine and isobutaldehyde at so low a temperature as 60°,² and C. Béis obtains isoindolinones by the reaction of phenylphthalimide with nascent magnesium alkyl halides.³

O. Carrasco and M. Padoa have examined the formation and decomposition of the indole nucleus by finely-divided nickel; this acts, in presence of hydrogen, as a hydrogenating agent at 200—250°, but at 300—330° it dehydrogenates methyl-*o*-toluidine to indole.⁴

A. Ellinger⁵ shows that the substance obtained by F. G. Hopkins and Cole on oxidising tryptophan⁶ with ferric chloride is not really a hitherto unknown hydroxyquinoline, but indole-3-aldehyde which may be synthesised from indole, chloroform, and caustic potash, although at the same time some 3-chloroquinoline is obtained.



The transformation of tryptophan into kynurenic acid in the organism is evidently of a similar type:



In a later paper, Ellinger and C. Flamand⁷ prove that the product of the action of chloroform and potash on scatole is β -chlorolepidine as had been supposed by Magnanini.⁸

Emil Fischer and C. Kaas have prepared a glycyilmethylindole,⁹

¹ *Annalen*, 1906, **350**, 1.

³ *Compt. rend.*, 1906, **143**, 430.

⁵ *Ber.*, 1906, **39**, 2515.

⁷ *Ber.*, 1906, **39**, 4388.

⁹ *Ibid.*, 1906, **39**, 1276.

² *Monatsh.*, 1906, **27**, 731.

⁴ *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 699.

⁶ *J. Physiol.*, 1903, **29**, 451.

⁸ *Ibid.*, 1884, **17**, 246; 1887, **20**, 2608.

and R. Pschorr and W. Karo¹ have isolated and hydrogenised *N*-methyl- β -naphthindole.

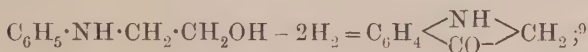
The molecular weight of indigotin in various solvents has been determined by E. Beckmann and W. Gabel²; the formation of double molecules was only observed in the case of the cryoscopic determination in a *p*-toluidine solution.

A number of patents have been taken for increasing the yield of indoxyl and indigotin in synthetic processes. The fusion of phenylglycine with alkali is generally unsatisfactory. Meister, Lucius, & Brünig add lead and sodium to a mixture of potassium and sodium hydroxides on fusion with potassium phenylglycine, and claim to raise the yield of indigotin to 40—50 per cent.³ The Basler Chemische Fabrik⁴ employ an intimate mixture of potassium and sodium hydroxides at 210—260°, whilst Léon Lilienfeld has patented an addition of slaked lime or magnesia to the fused alkali and subsequent heating in a current of ammonia at 150—300°.⁵

The Badische Anilin- und Soda-Fabrik obtain indigotindiacetic acid from anthranilodiacetic acid; from the former they obtain successively isatin-acetic and phenylglycine-*o*-carboxylic acids.⁶

The chlorination of indigotin forms the subject of two patents of the Badische Co.,⁷ and J. Schwarz describes 6:6'-dinitro- and diamino-indigotin which he obtains by using 4-nitro-2-aminobenzoic acid instead of anthranilic acid in the usual indoxyl reactions.⁸

The Badische Anilin- und Soda-Fabrik also obtain indoxyl by a new process, in that they fuse hydroxyethylaniline and its derivatives with alkalis,



and H. Decker and C. Kopp¹⁰ have observed the formation of indigotin by the alkaline oxidation of the addition product of quinoline and ethyl chloroacetate.

The so-called "thioindigo-red" which stands in the same relationship to indigotin that thiophen does to pyrrole, and is manufactured by Kalle and Co. has been examined by R. Wirther.¹¹ The formation of the substance from thiosalicylic acid is described by P. Friedländer.¹² Thiosalicylic and chloroacetic acids react quantitatively in presence of

¹ *Ber.*, 1906, **39**, 3140.

³ D.R.-P. 163039.

⁵ D.R.-P. 166447.

⁷ D.R.-P. 160187, 163280.

⁹ D.R.-P. 171172.

¹¹ *Färberzeitung*, **17**, 85.

¹² *Ber.*, 1906, **39**, 1060. Compare the following English patents (Kalle & Co.), 16100, 16101, 16907 of 1906.

² *Ibid.*, 2611.

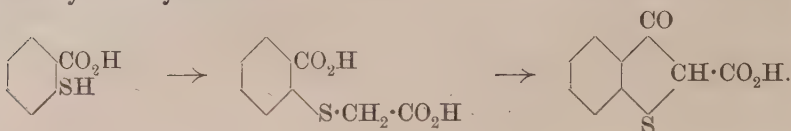
⁴ D.R.-P. 165691.

⁶ D.R.-P. 168292.

⁸ *Monatsh.*, 1905, **26**, 1255.

¹⁰ *Ber.*, 1906, **39**, 72.

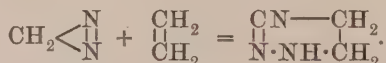
alkali; the further action of alkali furnishes a sulphur-analogue of indoxylcarboxylic acid:



The latter substance is readily oxidised in alkaline solution to thioindigotin, $C_{16}H_8O_2S_2$, which dissolves in chloroform with bluish-red colour and strong, yellowish-red fluorescence. The solution in concentrated sulphuric acid has an intense blue colour.

Pyrazole, Pyrazolone, and Indazole Derivatives.

E. Azzarello¹ finds that pyrazoline results from the direct addition of diazomethane to ethylene despite the statement of von Pechmann to the contrary.²



The formation of ethyl 4:5-dihydropyrazole-3:4:5-tricarboxylate observed by O. Silberrad and C. S. Roy, when ethyl diazoacetate spontaneously decomposes, is evidently due to the formation of ethyl fumarate or maleate, which then combines with undecomposed diazoacetic ester.³

L. Knorr and A. Köhler find that pyrazole readily gives 1-methylpyrazole methiodide which yields *sym.*-dimethylhydrazine on distillation with strong caustic potash solution.⁴

Further pyrazole syntheses have been effected by G. Minunni and G. Lazzarini,⁵ L. Berend and P. Herms,⁶ and J. B. Tingle and C. J. Robinson.⁷

Amongst pyrazolone syntheses, is to be noted the condensation of phenylhydrazine with ethyl alkylpropiolates by C. Moureu and I. Lazennec,⁸ for example, the same product is produced on condensing phenylhydrazine with ethyl amylpropiolate as with ethyl hexylacetate.

Mixed azo-compounds containing pyrazolones as components have been examined by A. Eibner and O. Laue⁹ and C. Bülow and F. Busse;¹⁰ whilst the condensation of phenylmethylpyrazolone with

¹ *Gazzetta*, 1906, **36**, i, 618.

² *Trans.*, 1906, **89**, 179.

³ *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 19, 136.

⁴ *J. pr. Chem.*, 1906, [ii], **74**, 112.

⁵ *Compt. rend.*, 1906, **142**, 1534.

⁶ *Ber.*, 1906, **39**, 3861.

⁷ *Ber.*, 1895, **28**, 885.

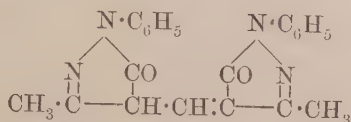
⁸ *Ber.*, 1906, **39**, 3257.

⁹ *Amer. Chem. J.*, 1906, **36**, 223.

¹⁰ *Ber.*, 1906, **39**, 2022.

aldehydes has afforded M. Betti and C. M. Mundici some interesting results.¹

Normally one molecule of an aldehyde forms a condensation product with two molecules of the pyrazolone, but with β -hydroxynaphth-aldehyde, β -naphthol is eliminated and a substance possessing the constitution



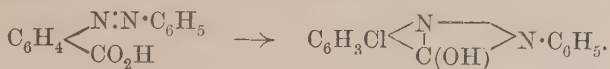
results.

A. Michaelis and A. Zilg find that phosphoryl chloride reacts in a different manner with aldehydo- and keto-bispyrazolones as compared with simple pyrazolones.² Whilst the pyrazolones furnish chloropyrazoles, the *bis*-compounds lose water, the aldehydo-compounds furnishing products which may be looked on as carbon analogues of rubazonic acid. A later paper by A. Michaelis and H. Schlecht³ shows that whereas 5- and 3-pyrazolones react readily with diazonium chlorides, this property is not shared by antipyrine and thiopyrine, although 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone may be subsequently methylated by the employment of dimethylsulphate.

A recent paper by Michaelis⁴ contrasts the action of nitrous acid on 5- and 3-pyrazolones, the former yield red unstable *isonitroso*-derivatives which easily furnish rubazonic acid; the green nitroso-derivatives of the 3-pyrazolones may be reduced to amino-compounds which give diazonium salts of remarkable stability.

M. Conrad and A. Zart⁵ have obtained good yields of 3-hydroxy-1-phenyl-5-pyrazolone by the condensation of phenylhydrazine and ethyl malonate in presence of sodium ethoxide; the compound has been already described by Michaelis.⁶

An interesting indazole synthesis is described by P. Freundler,⁷ who shows that benzene-*o*-azobenzoic acid condenses with phosphorus pentachloride to furnish chloro-3-hydroxy-2-phenylindazole.



P. Carré⁸ finds that a similar reaction takes place with *o*-hydrazobenzoic acid, a non-chlorinated product resulting (3-hydroxy-*o*-indazylbenzoic acid).

F. Bamberger and S. Wildi show that azoindazole results in 90 per

¹ *Gazzetta*, 1906, **36**, i, 178.

² *Ibid.*, 1954.

³ *Ber.*, 1906, **39**, 2282.

⁷ *Compt. rend.*, 1906, **142**, 1153.

² *Ber.*, 1906, **39**, 370.

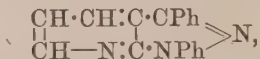
⁴ *Annalen*, 1906, **350**, 288.

⁶ *Ibid.*, 1892, **25**, 1506.

⁸ *Ibid.*, 1906, **143**, 54.

cent. yield when aminoindazole is oxidised by air in alkaline solution.¹

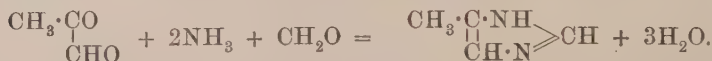
Structurally related to indazole are the compounds produced by G. Ortoleva.² When iodine is added to a solution of benzaldehyde-phenylhydrazone in pyridine solution, the hydriodide of a new base,



is produced. The phenyl attached to nitrogen can be oxidised to a carboxyl group and carbon dioxide eliminated from the resulting acid.

Iminazoles.

A. Windaus has continued his work on the formation of 4-methylglyoxaline by the action of ammoniacal zinc hydroxide on dextrose.³ The sugar is resolved into formaldehyde and glyceraldehyde, and the latter isomerising to methylglyoxal, the two aldehydes react with ammonia according to the following equation :

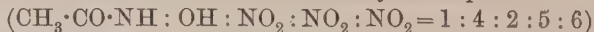


Confirmation of this view is afforded by the fact that addition of acetaldehyde causes the formation of a certain amount of 2 : 4-dimethylglyoxaline.

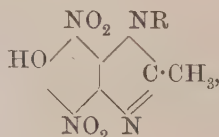
S. Gabriel⁴ has revised the work of Andreasch⁵ on the reaction between bromine and α -lactylcarbamide; the supposed "pyruvic ureide" possesses the formula $\text{C}_8\text{H}_8\text{O}_4\text{N}_4$, and is probably constituted thus :



R. Meldola describes a new trinitro-acetylaminophenol



produced by the energetic nitration of diacetyl-*p*-aminophenol.⁶ With primary amines, nitrous acid and water are eliminated and benz-iminazoles of the general formula :



produced

¹ *Ber.*, 1906, **39**, 4276.

² *Ber.*, 1906, **39**, 3886.

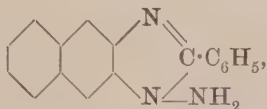
³ *Monatsh.*, 1902, **23**, 812.

⁴ *Gazzetta*, 1906, **36**, i, 473.

⁵ *Annalen*, 1906, **348**, 50, and **350**, 118.

⁶ *Trans.*, 1906, **89**, 1935.

Other benziminazoles are prepared by Otto Fischer and F. Limmer from 4-chloro-1:2-phenylenediamine¹ and by R. von Walther and A. Kessler from 4-nitro-2-aminodiphenylamine;² whilst H. Franzen has prepared an *N*-aminobenziminazole of the constitution:



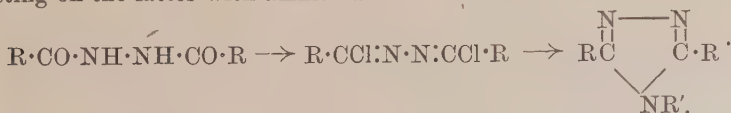
which only shows the reactions of an *as-sec.*-hydrazine in a very imperfect manner, many aldehyde reactions being absent.³

M. O. Forster and H. Grossmann have prepared nitrogen halides from camphoryl- ψ -carbamide,⁴ whilst the first author⁵ has also prepared diazoamino-derivatives of ψ -semicarbazino-camphor. These substances do not exhibit the usual tautomerism of mixed diazoamino-compounds; their absorption spectra are of considerable interest.

Triazoles.

The recognition of the so-called "trimethintriazimid" of Curtius (which Hantzsch and Silberrad took for dihydrotetrazine) as 1-*N*-amino-3:4-triazole is the most interesting fact to be recorded in this class of compounds. C. Bülow⁶ shows that this substance has a free amino-group, in that it condenses with ethyl diacetylsuccinate to form a compound containing both pyrrole and triazole rings, and the production of triazole from this compound by the action of nitrous acid is no longer surprising, neither is the fact that it yields only a monoacetyl derivative. The discussion between Stollé⁷ and Ruhemann⁸ as to the constitution of the condensation product with benzaldehyde loses its interest; the substance obtained is simply a hydrazone.

R. Stollé, A. Weindel, and A. Bambach⁹ synthesise triazoles by converting symmetrical diacylhydrazines into imino-chlorides and reacting on the latter with ammonia and other bases.



O. Dimroth, E. Frisoni, and J. Marshall condensed phenylazo-imide with ketones in the hope of effecting a direct triazole synthesis.¹⁰

¹ *J. pr. Chem.*, [ii], **74**, 57.

² *Ibid.*, 1906, [ii], **73**, 545.

³ *Ibid.*, 222.

⁴ *Ibid.*, 826.

⁵ *J. pr. Chem.*, 1906, [ii], **74**, 1, 13.

⁶ *Ibid.*, 188, 241.

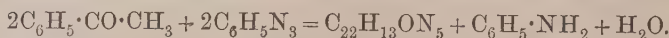
⁷ *Trans.*, 1906, **89**, 402.

⁸ *Ber.*, 1906, **39**, 2618, 4106.

⁹ *Ibid.*, 1228.

¹⁰ *Ber.*, 1906, **39**, 3920.

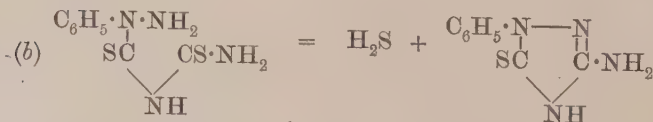
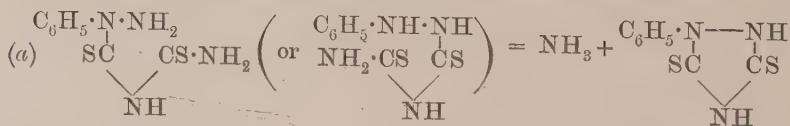
The reaction followed a different course according to the equation



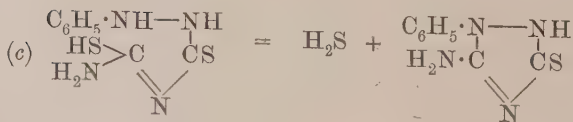
The product of the reaction furnishes 4-amino-1 : 5-diphenyl-1 : 2 : 3-triazole on reduction, which can be reconverted into the compound $\text{C}_{22}\text{H}_{13}\text{ON}_5$ by diazotisation, coupling with ethyl benzoylacetate, and removal of the carbethoxy-group. It is evident that in the original reaction half of the phenylazoimide plays the part of a diazotising agent.

O. Dimroth and H. Aickelin¹ have obtained 5-triazolone from methyl 1-phenyl-5-triazolone-4-carboxylate by introducing two nitro-groups and subsequent complete hydrolysis; the substance was isolated as its *p*-tolueneazo-derivative. Further triazolone derivatives are described by O. Dimroth and L. Taub² and T. Curtius and J. Thompson.³

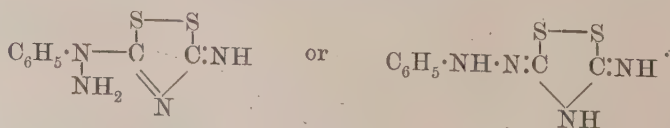
E. Fromm and K. Schneider⁴ have studied the action of phenylhydrazine on perthiocyanic acid; the expected phenylaminodithiobiuret was not isolated, but in its place three compounds of the formulæ $\text{C}_8\text{H}_8\text{N}_4\text{S}$, $\text{C}_8\text{H}_7\text{N}_3\text{S}_2$ and $\text{C}_8\text{H}_8\text{N}_4\text{S}_2$. The first two compounds contain rings made up of two carbon and three nitrogen atoms owing to the elimination of hydrogen sulphide and ammonia respectively from the initially formed phenylamino- (or anilino-) dithiobiuret.



or



The first formula (b) is preferred, whilst the compound $\text{C}_8\text{H}_8\text{N}_4\text{S}_2$ is looked on as having one of the two constitutions:



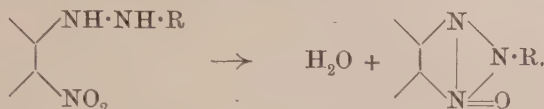
¹ *Ber.*, 1906, **39**, 4390.

² *Ibid.*, 3912.

⁴ *Annalen*, 1906, **348**, 174.

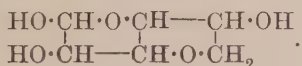
³ *Ibid.*, 4140.

A. Werner and W. Peters¹ have obtained nitrosoazo-compounds from *o*-chloronitro-compounds and phenylhydrazine; E. Grandmougin² has obtained similarly constituted substances by the reduction of *o*-nitroazo-compounds with sodium hyposulphite; the reaction in both cases may be expressed in the following manner:

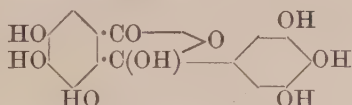


Furan Group.

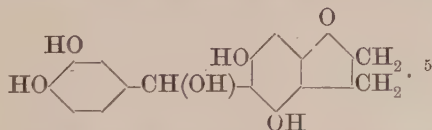
No important syntheses have been effected in this group, but several compounds have been studied containing a ring of one oxygen and four carbon atoms. E. Vongerichten and F. Müller³ consider glycosan to be



J. Dekker assigns the constitution

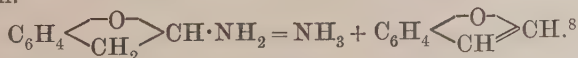


to tannin,⁴ whilst S. von Kostanecki and V. Lampe consider that catechin is most probably to be represented by the formula



Whilst W. J. Hale, W. D. McNally, and C. J. Pater⁶ have successfully converted ethyl pyromucate into tertiary alcohols (furyl-dialkyl carbinols) by aid of magnesium alkyl halides, the attempts of S. Courant and S. von Kostanecki⁷ to prepare flavanones from β -furyl-chromanones have simply resulted in the opening of the furan ring.

R. Stoermer and W. König have succeeded in isolating 2-amino-coumaran, but all attempts at making 1-aminocoumaran have been unsuccessful, the substance losing ammonia at the moment of its formation.



¹ Ber., 1906, 39, 185. ² Ibid., 3931. ³ Ibid., 241. ⁴ Ibid., 2497.

⁵ Compare A. G. Perkin, Trans., 1902, 81, 1160.

⁶ Amer. Chem. J., 1906, 35, 68. ⁷ Ber., 1906, 39, 4031.

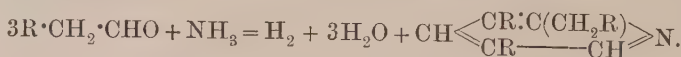
⁸ Ibid., 4927.

The "fulgides" mentioned in last year's Report have been further examined by H. Stobbe with very interesting results as to the relationship between colour and constitution.¹

Pyridine and Piperidine.

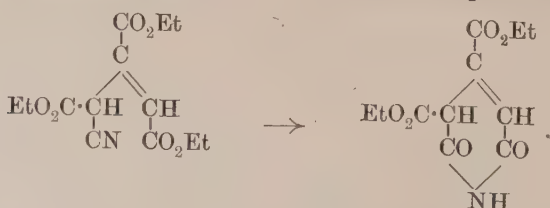
J. von Zawidzki has determined some of the constants of carefully purified pyridine, and states that its melting point is $+42^{\circ}$,² whilst D. Vorländer gives a method for the purification of commercial piperidine which contains unsaturated bases.³

With regard to syntheses in the pyridine series, A. E. Tschitschibabin⁴ finds that the action of ammonia on aldehydes always consists of a termolecular condensation according to the general equation



P. I. Petrenko-Kritschenko and N. Zoneff show that when methyl acetonedicarboxylate and benzaldehyde are condensed in the presence of ammonia, the product is not a tetrahydropyrene derivative as previously described, but methyl 2:6-diphenylpiperidone-3:5-dicarboxylate.⁵

H. Rogerson and J. F. Thorpe have prepared new citrazinic acid derivatives.⁶ The sodium derivative of ethyl cyanoacetate and ethyl oxalacetate give the sodium derivative of ethyl α -cyanoaconitate. Ethyl α -cyanoaconitate is transformed into ethyl 2:6-dihydroxypyridine-4:5-dicarboxylate by cold concentrated sulphuric acid:



The preparation of several other pyridine derivatives is described in this paper.

The etherification of γ -pyridone with diazomethane and diazoethane is interesting; A. Peratoner and E. Azzarello find that a mixture of 4-alkyloxypyridine and *N*-alkyl pyridone is produced in both cases.⁷

¹ *Ber.*, 1906, **39**, 292, 761; *Annalen*, 1906, **349**, 333.

² *Chem. Zeit.*, 1906, **30**, 299.

³ *Annalen*, **345**, 277.

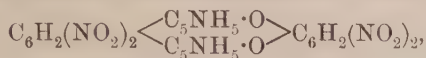
⁴ *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1229; *Abstr.*, 1906, **90**, i, 451.

⁵ *Ber.*, 1906, **39**, 1358.

⁶ *Trans.*, 1906, **89**, 631.

⁷ *Atti R. Accad. Lincei*, 1906, [v], **15**, i, 139.

F. Reitzenstein and J. Rothschild find that 1:5-dichloro-2:4-dinitrobenzene and pyridine yield a condensation product,

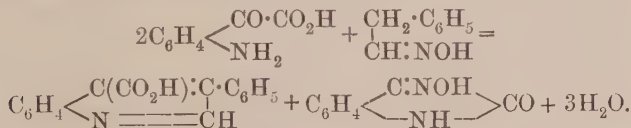


which decomposes on boiling with hydrochloric acid, a substance having the composition of 2:4-dinitro-5-hydroxyphenylpyridinium hydroxide being produced.¹

Quinoline.

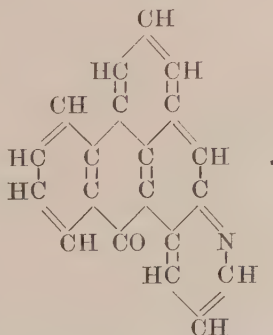
Some interesting quinoline syntheses have been effected in the past year. L. J. Simon and C. Mauguin condense benzyldiene- β -naphthylamine and ethyl oxalacetate to ethyl phenyldihydronaphthaquinoline-dicarboxylate, which is readily oxidised to the naphthaquinoline derivative.²

H. Hübner³ has obtained β -phenyleinchoninic acid by the condensation of isatic acid with phenylacetaldoxime



This work, which is a continuation of that of W. Pfitzinger,⁴ has been further developed by B. Mulert.⁵

Alizarin-blue is converted by mild oxidation to a yellow *ortho*-quinone, reconverted to the blue by reduction, and furnishes alizarin-blue amide with ammonia.⁶ Whilst β -aminoalizarin condenses with glycerol and sulphuric acid to give alizarin-blue by the ordinary Skraup reaction, β -aminoanthraquinone condenses with two molecules of glycerol to form benzanthronequinoline.⁷



¹ *J. pr. Chem.*, 1906, [ii], **73**, 257.

² *Compt. rend.*, 1906, **143**, 427, 466.

³ *Ber.*, 1906, **39**, 982.

⁴ *J. pr. Chem.*, 1897, [ii], **56**, 283, and 1902, [ii], **66**, 263.

⁵ *Ber.*, 1906, **39**, 1901.

⁶ Farbenfabriken Bayer, D.R.-P. 171836.

⁷ B.A.S.F. ; D.R.-P. 171939.

The degradation of the quinoline nucleus by hydrogen and reduced nickel at 260—280° has been found to yield 2-methylindole, methyl *o*-toluidine, and *o*-toluidine (M. Padoa and A. Carughi).¹

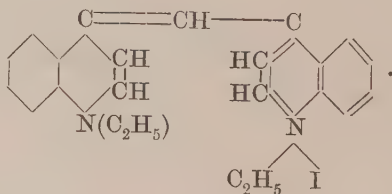
H. Meyer, in an examination of kynurine derivatives, finds that 4-chloroquinoline and sodium alkyloxides yield 4-alkyloxyquinolines;² the methyl compound is transformed into the ψ -methyl ether at 300—310°, whilst the ethyl ether undergoes a similar change at 360°.

A. Benrath³ finds that addition of benzaldehyde to quinoline takes place on exposure to sunlight, *N*-benzoyl-1:2-dihydroquinoline being produced. When, however, quinaldine is substituted for the quinoline, 2- β -hydroxy- β -phenylethylquinoline results. Generally, the condensation of aldehydes with quinaldine takes place with elimination of water, and the colouring properties of the substances formed have been examined by E. Noelting and E. Witte.⁴ These authors find that the product from quinaldine and protocatechuic aldehyde,



is both a basic and a mordant dyestuff. The nearly related quinonaphthalones obtained by condensation with naphthalic anhydride have been studied by A. Eibner and M. Löbering.⁵

W. König⁶ considers that the blue diethylecyanine is represented constitutionally by the formula



If so, the substance shows some analogy with the pyridine dyes obtained by the same author from furfuraldehyde.⁷

F. Fichter and R. Boehringer⁸ have prepared a substance containing both quinoline and indole nuclei, two carbon atoms being common to each group; this they name quindoline. For its preparation, ethyl bis-*o*-nitrobenzylmalonate is boiled with alcoholic caustic soda, ethyl

¹ *Atti R. Accad. Lincei*, 1906, [v], 15, ii, 113.

² *Monatsh.*, 1906, 27, 255.

⁴ *Ber.*, 1906, 39, 2749.

⁶ *J. pr. Chem.*, 1906, [ii], 73, 100.

⁸ *Ber.*, 1906, 39, 3932.

³ *J. pr. Chem.*, 1906, [ii], 73, 383.

⁵ *Ibid.*, 2215.

⁷ *Ibid.*, 1905, [ii], 72, 555.

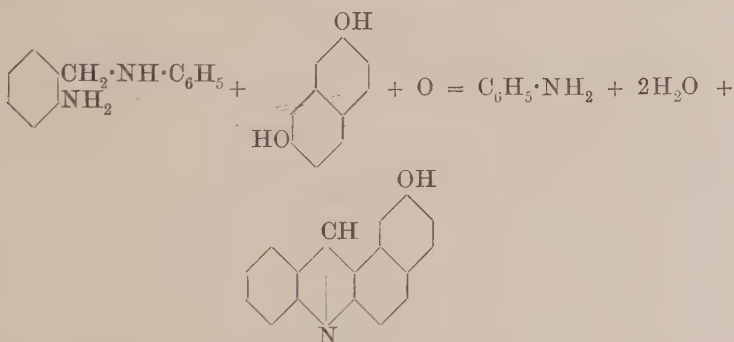
alcohol and carbon dioxide are removed, and the resulting *bis-o*-nitrobenzylmethane condenses to dihydroxyquindoline:



The two hydroxy-groups may be successively removed by the action of phenylhydrazine, that attached to nitrogen being first eliminated. Quindoline (m. p. 247—248°) is a base which yields quaternary ammonium compounds, from these *pseudo*-bases are produced by the action of alkalis.

Acridine.

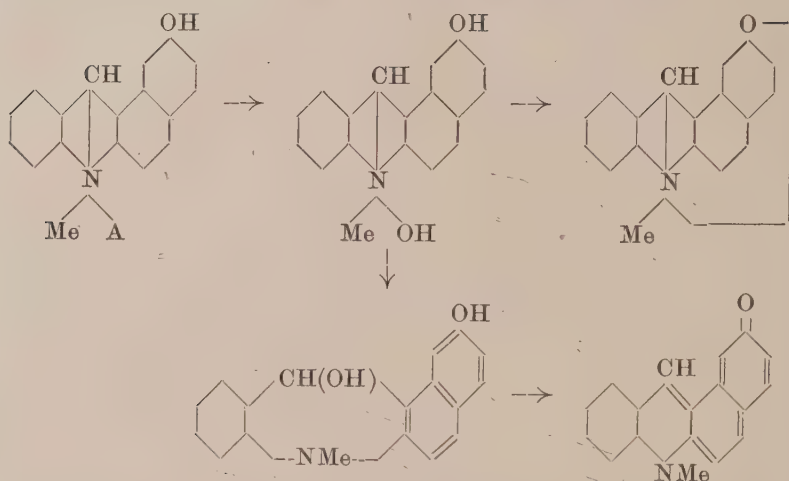
F. Ullmann has, in conjunction with E. Bühler, H. W. Ernst, W. Denzler and J. Broido, extended the number of acridine syntheses,¹ and C. Baezner, J. Gueorguieff, and A. Gardiol have prepared hydroxylated phenonaphthacridines.² The compound obtained by Baezner and Gardiol on condensation of *o*-aminobenzylaniline with 2:7-dihydroxynaphthalene:



exhibits interesting behaviour. On decomposing its quaternary acridinium salts with ammonia, a dark blue product, insoluble in alkalis, is produced; the authors think this may be an internal anhydride resulting from the removal of water from the ammonium and phenolic hydroxyl group; the writer of this report would like to point out the possibility of the substance being quinonoid in structure and derived from the carbinol *pseudo*-base. The two views may be represented in the following manner:

¹ *Zeit. Farb. Text. Ind.*, 1905, **4**, 521; *Ber.*, 1906, **39**, 298, 356, 4332.

² *Ber.*, 1906, **39**, 2438, 2623.



The latter view receives support from the work of A. E. Dunstan and J. T. Hewitt on the acridinium compounds of chrysaniline¹ and chrysophenol²; the corresponding *pseudo*-bases have only a transitory existence and yield quinonoid anhydro-bases.

Various derivatives of 9-phenylacridine have been prepared during the past year by H. Decker, C. Schenk,³ and A. Schmid,⁴ as well as by A. E. Dunstan, with R. O'F. Oakley⁵ and J. A. Stubbs.⁶

S. Cuttitta has obtained 2-*o*-nitro-*p*-toluidino-3:5-dinitrobenzoic acid by the condensation of 2-chloro-3:5-dinitrobenzoic acid with *o*-nitro-*p*-toluidine, and has shown that it condenses in presence of strong sulphuric acid to 1:3:6-trinitro-7-methylacridone.⁷

The dinaphthacridines resulting from the action of chlorides of the type $R \cdot CHCl_2$ on α - and β -naphthylamines, separately or mixed, have been examined by A. Senior and P. C. Austin,⁸ whilst di-acridine (quinacridine, &c.) derivatives have been prepared by S. von Niementowski,⁹ F. Ullmann, and R. Maag,¹⁰ and C. Baezner.¹¹

Diazines.

But little has to be recorded with respect to *o*-diazines; J. Thiele and O. Günther¹² have worked out a method for the preparation of *o*-phthalaldehyde in quantity, and the former and K. G. Falk¹³ have studied the products formed on condensation with bases. With phenyl-

¹ *Trans.*, 1906, **89**, 482.

⁴ *Ibid.*, 933.

⁷ *Gazzetta*, 1906, **36**, i, 325.

⁹ *Ber.*, 1906, **39**, 385.

¹² *Annalen* 1906, **347**, 107.

² *Ibid.*, 1472.

⁵ *Ibid.*, 977.

⁸ *Trans.*, 1906, **89**, 1387.

¹⁰ *Ibid.*, 1693.

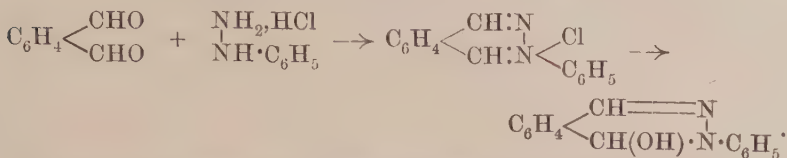
¹³ *Ibid.*, 112.

³ *Ber.*, 1906, **39**, 748.

⁶ *Ibid.*, 2402.

¹¹ *Ibid.*, 2656.

hydrazine hydrochloride a quaternary ammonium chloride is formed which yields a *pseudo*-base on treatment with alkali:



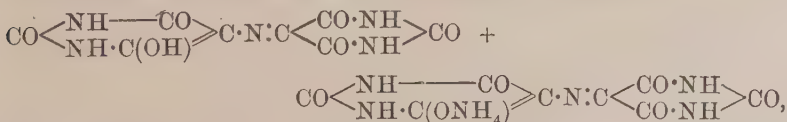
It is a very remarkable fact that an eight-membered ring is *not* produced by the interaction of *o*-phthalaldehyde and *o*-phenylenediamine;

o-benzylenebenziminazole, $\begin{array}{c} \text{CH}_2\text{---N}\cdot\text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N} \end{array}$, being formed instead.

Amongst the *m*-diazines, many syntheses of barbituric acid and its derivatives (especially 5:5-dialkylbarbituric acids) must be noted, these have formed the subject matter of many patents. The processes usually consist in a condensation of a derivative of malonic acid (ester, acid chloride, amide, or nitrile) with a derivative of carbonic acid, and the greater number of patents have been taken by the Farbenfabriken vorm. F. Bayer & Co. and E. Merck.

Other syntheses of pyrimidine derivatives are due to T. B. Johnson in conjunction with G. A. Menge,¹ E. V. McCollum,² C. O. Johns³ and McCollum, Johns and F. W. Heyl.⁴ Many of these syntheses result in the production of cytosine (6-amino-2-oxypurine) derivatives, and may be illustrated by Johnson and McCollum's preparation of 5-hydroxycytosine. Ethyl formate and ethyl ethylglycollate are condensed by sodium to the metallic derivative of ethyl β -hydroxy- α -ethoxyacrylate, $\text{NaO}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{CO}_2\text{Et}$. The latter substance reacts with the hydrobromide of ψ -ethylthiocarbamide to furnish 6-oxy-5-ethoxy-2-ethylthiolpyrimidine, which heated with hydrochloric acid to 150° is hydrolysed to isobarbituric acid (2:5:6-trihoxypurine). This differs from 5-hydroxycytosine in having a hydroxyl- instead of an amino-group in position 6.

R. Mühlau and H. Litter⁵ consider that purpuric acid and murexide are most probably represented by the respective formulæ:



whilst O. Kühling and O. Kaselitz⁶ have examined the condensation of *N*-substituted *o*-diamines with alloxan and its derivatives.

R. Behrend and H. Friedrich⁷ find that dialuric acid forms only

¹ *J. Biol. Chem.*, 1906, **2**, 105.

² *Ibid.*, 1906, **4**, 437.

³ *Ibid.*, 805.

⁴ *Amer. Chem. J.*, 1906, **36**, 136, 149, 160.

⁵ *J. pr. Chem.*, 1906, [ii], **73**, 449.

⁶ *Ber.*, 1906, **39**, 1314.

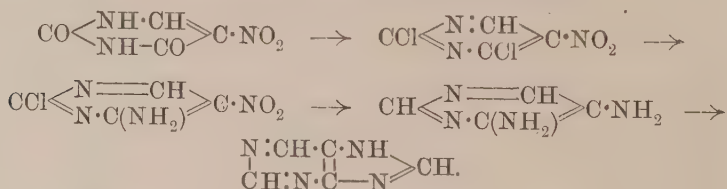
⁷ *Annalen*, 1906, **344**, 1.

one series of salts, $C_4H_3O_4N_2M$, and further, that its acetyl and benzoyl (mono-) derivatives are also monobasic acids.

Before passing on to the purine group with its conjugated pyrimidine and glyoxaline rings, we may note that various quinazoline syntheses have been effected by M. T. Bogert and his co-workers.¹

Purine Group.

O. Isay² gives a synthesis of purine starting with Behrend's 5-nitrouracil.³ The substance is converted into 2:4-dichloro-5-nitropyrimidine by phosphoryl chloride; in this compound the 4-chlorine atom may be replaced by the amino-group by ammonia in the cold. If the resulting 2-chloro-5-nitro-4-aminopyrimidine is reduced with hydriodic acid and phosphonium iodide, 4:5-diaminopyrimidine results, which may then be condensed with formic acid to purine:



A new synthesis of guanine is patented by E. Merck,⁴ and other syntheses in the purine group are described by W. Traube in conjunction with W. Nithack⁵ and F. Winter.⁶

Emil Fischer and F. Ach⁷ describe the transformation of caffeine into paraxanthine, theobromine, and theophylline. Phosphorus pentachloride reacts with caffeine to replace hydrogen in position 8 by chlorine, but then successively converts the methyl into chloromethyl groups. On hydrolysis, the chloromethyl groups are eliminated as formaldehyde, and the resulting chloroxanthine derivative may be reduced.

G. Denicke⁸ has obtained several compounds containing five-membered rings by oxidising uric acid in presence of ammonia.

J. K. Wood has quite recently⁹ determined the affinity constants of xanthine and a number of its methyl derivatives. The dissociation constants of xanthine, heteroxanthine, theobromine, theophylline, paraxanthine, and caffeine, were determined, regarding the substance examined as (a) a base, (b) an acid. Caffeine, as might be expected,

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 94, 207, 884, 1449.

² *Ber.*, 1906, **39**, 250.

³ *Annalen*, 1887, **240**, 4; 1889, **251**, 238.

⁴ D.R.-P., 162336.

⁵ *Ber.*, 1906, **39**, 227.

⁶ *Arch. Pharm.*, 1906, **244**, 11.

⁷ *Ber.*, 1906, **39**, 423.

⁸ *Annalen*, 1906, **349**, 269.

⁹ *Trans.*, 1906, **89**, 1831.

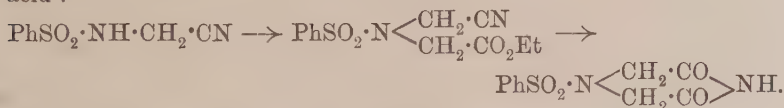
exhibits no acid properties; the relationships exhibited by theobromine and the isomeric paraxanthine are, however, remarkable. One would have expected the former to behave as the stronger acid, having an imino-group joined on both sides to carbonyl; the reverse is the case, the value of k_a being about twenty times as great for paraxanthine as for theobromine.

A number of ureides have been examined; barbituric acid and 5-ethylbarbituric acid are both stronger than acetic acid, but 5:5-diethylbarbituric acid is extremely weak, the value of k_a being but one-thousandth that of the monoethyl compound. The conclusion is drawn that the hydrogen atoms of the methylene group in barbituric acid are responsible for furnishing hydrogen ions.

Paradiazines.

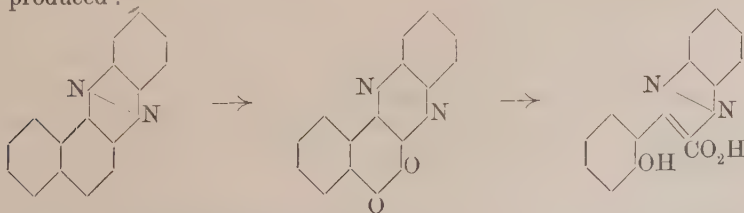
Strictly speaking, the α - β' -diketopiperazines are p -diazine derivatives, but on account of their near relationship to the polypeptides will not be treated amongst the heterocyclic compounds.¹

A new synthesis of $\alpha\alpha'$ -diketopiperazines has been effected by T. B. Johnson and E. V. McCollum.² Benzenesulphonylaminoacetonitrile is condensed with ethyl chloroacetate, the resulting compound being then successively treated with caustic soda and hydrochloric acid:



In the phenazine group, P. Barbier and P. Sisley continue their study of *s*- and *as*-phenosafranines³ and two interesting papers in the naphthaphenazine group have appeared from O. Fischer in conjunction with E. Schindler⁴ and K. Arntz⁵ respectively.

In the first of these communications it is shown that naphthaphenazine yields a diketo-compound by oxidation with chromic acid; on fusion of the *o*-quinone with caustic soda a hydroxycarboxylic acid is produced:



¹ See Emil Fischer, *Ber.*, 1906, **39**, 530, 752, 3981.

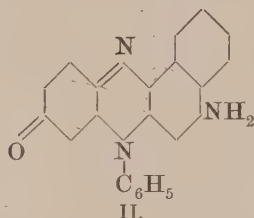
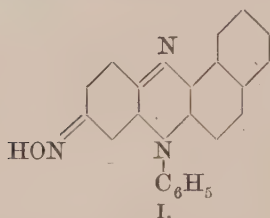
² *Amer. Chem. J.*, 1906 **35**, 54.

³ *Bull. Soc. chim.*, 1906, [iii], **35**, 858, 1278.

⁴ *Ber.*, 1906, **39**, 2238.

⁵ *Ibid.*, 3807.

In the second paper, it is shown that the supposed oxime of isorosindone is in reality an amino-compound; the formulæ of the substance expected (I), and of that actually obtained (II), are given;



Azines derived from quinoline are described by W. Meigen and E. Nottebohm,¹ and from anthraquinone by the Farbenfabriken vorm. F. Bayer & Co.²

Triazines and Tetrazines.

A. Hantzsch has examined the behaviour of cyanuric acid as a *pseudo*-acid,³ whilst papers dealing with tetrazines have appeared from T. Curtius and J. Thompson,⁴ and Curtius, A. Darapsky, and E. Müller.⁵ These deal with the relationships existing between bisdiazio-, *pseudo*-diazio-, and dihydro-tetrazine compounds; but in view of Bülow's proof of an aminotriazole formula for the so-called "dihydropotetrazine" evidently need revision. Bülow,⁶ points out that the transformations of "bisdiazooacetic acid" are perfectly explicable if formulated as $\text{HO}_2\text{C} \cdot \text{C} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$; the isomerisation to aminotriazoledicarboxylic acid only necessitates an addition and subsequent elimination of a molecule of water, whilst the hydrolysis to two molecules of oxalic acid and two molecules of hydrazine is obvious from the formula.

The discussion between Ruhemann and Stollé has been already referred to.

Pyrone and Allied Compounds.

A method for determining the constitution of the hydroxyl-derivatives of pyrone has been devised by A. Peratoner⁷; the substances are alkylated by diazohydrocarbons of the fatty series before being submitted to fission by baryta. Thus Peratoner and

¹ Ber., 1906, **39**, 744.

² D.R.-P. 167255, 170562.

³ Ber., 1906, **39**, 189.

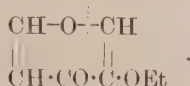
⁴ Ibid., 3398.

⁵ Ibid., 3410, 3776.

⁶ Ibid., 4106.

⁷ Gazzetta, 1906, **36**, [i], 1.

R. Spallino¹ find that the ethyl ether of pyromeconic acid yields a formate and ethoxyacetone with baryta,

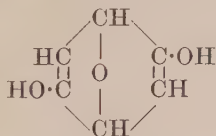


the ketone being readily isolated as the *p*-nitrophenylhydrazone.

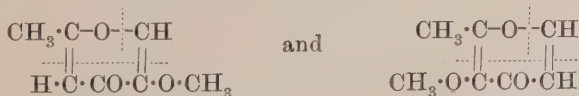
Applying the same method to the hydroxycomenic acid described in 1881 by Reibstein,² and subsequently obtained by the action of hydrogen peroxide on meconic acid by Collie and Tickle,³ Peratoner and V. Castellana⁴ show that it must be 2:3-dihydroxypyrene-6-carboxylic acid, since its trimethyl derivative furnishes acetylcarbinol methyl ether on fission.

For the determination of the constitution of comenic acid, the method of fission will not distinguish between 3-hydroxypyrene-2-carboxylic acid and 3-hydroxypyrene-6-carboxylic acid. But a comparison of the dissociation constants of comenic and comanic acids by Peratoner and F. C. Palazzo,⁵ has shown that the latter is the stronger acid of the two. Ostwald showed that benzoic acid is a stronger acid than *p*-hydroxybenzoic acid, but weaker than salicylic acid, and hence comenic acid is most probably the 3-hydroxy- γ pyrene-6-carboxylic acid.

Maltol, identical with the larixinic acid of Stenhouse, has now been referred to the pyrene group. The formula—



assigned to this substance by Brand,⁶ is unsatisfactory as only mono-acyl derivatives can be prepared. A. Peratoner and A. Tamburello⁷ find that it yields only a monomethyl ether with diazomethane, and this ether undergoes fission with baryta, furnishing formic and acetic acids and acetylcarbinol methyl ether. Such behaviour is consistent with one of the two following formulæ,



of which the second is the more probable, in that maltol differs from

¹ *Gazzetta*, 1906, **36**, i, 14.

² *Trans.*, 1902, **81**, 1004.

⁵ *Ibid.*, 7.

⁷ *Gazzetta*, 1906, **36**, i, 33.

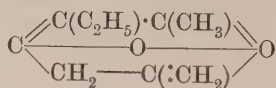
² *J. pr. Chem.*, [ii], **24**, 286.

⁴ *Gazzetta*, 1906, **36**, i, 21.

⁶ *Ber.*, 1894, **27**, 806.

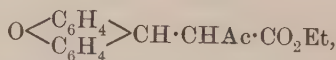
its lower homologue, pyromeconic acid, in not reacting with amyl nitrite, diazonium salts, sulphuryl chloride or iodic acid.

A. W. Bain¹ has acted on the disodium derivative of dimethylpyrone with ethyl iodide, obtaining thereby a mixture of dimethylethylpyrone and dimethyldiethylpyrone. But unless absolute alcohol and perfectly dry materials are used, an isomeride of dimethylethylpyrone is produced, to which the formula



has been assigned.

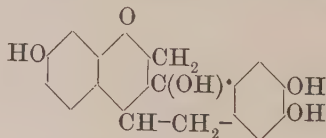
E. E. Blaise and H. Gault² publish a synthesis of alkylpyrandicarboxylic acids, starting with the condensation products of aldehydes and ethyl oxalacetate, and R. Fosse³ has continued his work on the oxonium salts obtained by the oxidation of pyran derivatives. He further finds that xanthidrol condenses with β -diketones and analogously constituted compounds to form derivatives of which ethyl xanthylacetoacetate,



may be taken as typical.⁴

C. Bülow⁵ and his co-workers have prepared several new anhydropyranol compounds, whilst S. von Kostanecki has continued his work in the flavonol series and, jointly with V. Lampe and J. Tambor, effected the synthesis of morin.⁶

Concerning other natural dye-stuffs, the appearance of two papers by J. Herzig and J. Pollak⁷ must be mentioned; these authors think that brazilin most probably possesses the constitution,



The constitution of euxanthone, the product of the hydrolysis of Indian-yellow, has been definitely settled by its synthesis. F. Ullmann and L. Panchaud,⁸ condense 2-chloro-6-methoxybenzoic acid and the monomethyl ether of quinol, using copper powder as catalyst; on treatment of the resulting 2-phenoxy-6-methoxybenzoic acid

¹ *Trans.*, 1906, **89**, 1224.

² *Compt. rend.*, 1906, **142**, 452.

³ *Bull. Soc. chim.*, 1906, [iii], **35**, 1005; *Compt. rend.*, 1906, **142**, 1543.

⁴ *Compt. rend.*, 1906, **143**, 239.

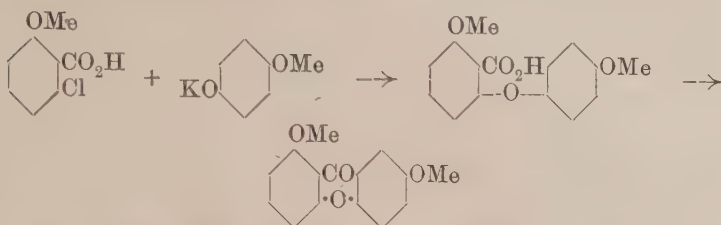
⁵ *Ber.*, 1906, **39**, 214, 850, 2027, 3664.

⁶ *Ber.*, 1906, **39**, 625.

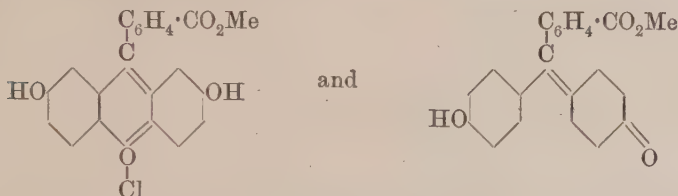
⁷ *Ibid.*, 265, and *Monatsh.*, 1906, **27**, 743.

⁸ *Annalen*, 1906 **350**, 108.

with strong sulphuric acid, the dimethyl ether of euxanthone is produced :



Several papers have appeared on derivatives of fluoran, A. G. Green and P. E. King¹ obtaining an oxonium chloride of a methyl ester of quinolphthalein by treating a solution of the latter with zinc chloride in hot methyl alcohol with hydrogen chloride. To this substance and the quinonoid ester obtained from phenolphthalein they ascribe the respective formulæ,



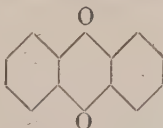
E. Noelting and K. Dziewoński² find that whilst *aporhodamine* ethyl ester yields *aporhodamine* on treatment with an alkali, a colourless ethylated carbinol base is produced by employing alcoholic potash, and alcoholic ammonia produces a colourless imide.

O. Silberrad³ has produced fluorescent substances by the condensation of mellitic and pyromellitic acids with resorcinol, and concludes from the examination and analyses of a number of derivatives that fluorescence is not necessarily conditioned by tautomerism.

Unclassified Cyclic Compounds.

As usual, a very large number of papers have appeared dealing with heterocyclic compounds containing nitrogen, oxygen, and sulphur in the ring ; of these, only a few which have especial interest can be noticed.

F. Ullmann and A. Stein have obtained *o*-diphenylene dioxide,



¹ *Ber.*, 1906, **39**, 2365

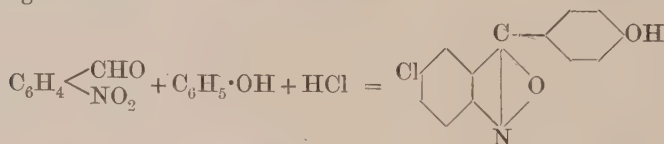
² *Ibid.*, 2744.

³ *Trans.*, 1906, **89** 1787.

by elimination of water from *o*-dihydroxydiphenyl ether, the dimethyl ether of the latter compound being obtained by heating a mixture of bromoanisole, guaiacol, and potassium hydroxide in presence of copper powder.¹ Di-2:3-naphthylene dioxide has also been examined by these authors as well as by A. A. Neil.²

The corresponding phenothioxin has been prepared by F. Mauthner, who prepares a nitrocarboxylic acid of this substance by condensation of 4-chloro-3:5-dinitrobenzoic acid with thiocatechol. The nitro-group is subsequently eliminated by reduction and the diazo-reaction, the carboxylic group by heating.³

T. Zincke and K. Siebert have published a very interesting synthesis of anthroxan (anthranil) derivatives;⁴ they find that *o*-nitrobenzaldehyde and phenols condense in presence of hydrochloric acid in the following manner:



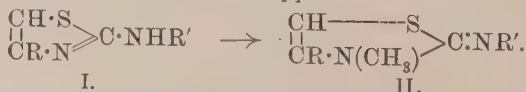
The substance produced was first isolated by Guyot and Haller, who, however, assigned to it the constitution of a chlorohydroxy-acridone.⁵

R. Stollé and K. Thomae⁶ find that dibenzoylhydrazide reacts with phosphorus pentachloride, yielding an imide chloride,

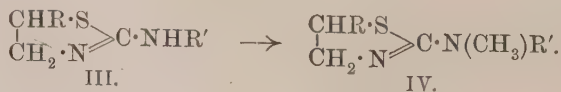


and a certain amount of 2:5-diphenyl-1:3:4-oxadiazole. The former substance reacts with primary amines, yielding 1:3:4-triazoles; the reaction has been extended by Stollé and his pupils by employing substituted dibenzoylhydrazides.

G. Young and S. I. Crookes⁷ have methylated several thiazoles of the type I, obtaining derivatives of type II:



On the other hand, they confirm the results obtained by Prager,⁸ who found that aminodihydrothiazoles (formula III) furnish methyl derivatives of type IV:



¹ *Ber.*, 1906, **39**, 622.

² *Ibid.*, 1905, **38**, 1411; 1906, **39**, 1840.

³ *Bull. Soc. chim.*, 1906 [iii], **31**, 350.

⁴ *Trans.*, 1906, **89**, 59.

⁵ *Ibid.*, 1059.

⁶ *Ibid.*, 1906, **39**, 1930.

⁷ *J. pr. Chem.*, 1906, [ii], **73**, 288.

⁸ *Ber.*, 1889, **22**, 1142, 2984.

von Pechmann stated the rule that when mixed amidines are alkylated, the alkyl group attaches itself to the more negative nitrogen atom, and the results obtained by Young and Crookes prove that this is applicable to cyclic as well as open-chain amidines.

Alkaloids.

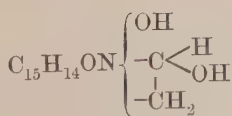
Amongst new alkaloids the anagyrine of G. Goessmann,¹ and hordenine of E. Léger² are to be recorded. The former, obtained from *Anagryis fetida*, has been assigned the formula $C_{15}H_{22}ON_2$, but it is possibly a mixture. Hordenine occurs in malt germs and has also been examined by O. Gaebel;³ both his results and those of Léger agree with the formula,



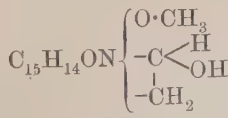
A. Ladenburg⁴ announces the complete synthesis of coniine. Whilst natural coniine gives a rotatory value $[\alpha]_D 15.6^\circ$, the synthetical reputed coniine gave $[\alpha]_D 18.3^\circ$, and the slight difference was ascribed to an admixture of "isoconiine" in the synthetical base. It now appears that the artificial product is really a stereoisomeride of coniine into which it may be transformed by heating for many hours at $290-300^\circ$ and subsequent distillation. The base thus obtained agrees with coniine in boiling at $164-166^\circ$, and giving the value $[\alpha]_D 15.67^\circ$.

A Pictet⁵ has published two *résumés* of the work on the tobacco alkaloids, whilst M. Freund and H. H. Reitz⁶ have examined the behaviour of cotarnine towards the Grignard reagents. The reactions observed are reconcilable with the usually received cotarnine formula, but cyanocotarnine appears to be a quaternary ammonium cyanide.

The chemistry of the opium alkaloids has engaged a great amount of attention, and the relationship of the alkaloids morphine, codeine, and thebaine may be taken as fully established. The bases in question may be written in the following manner :



Morphine.



Codeine.

¹ *Arch. Pharm.*, 1906, **244**, 20.

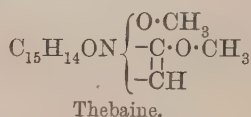
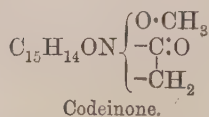
² *Compt. rend.*, 1906, **142**, 108 ; **143**, 234.

³ *Arch. Pharm.*, 1906, **244**, 435.

⁴ *Ber.*, 1906, **39**, 2486.

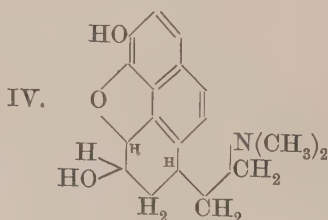
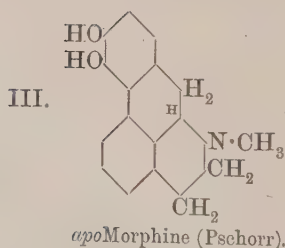
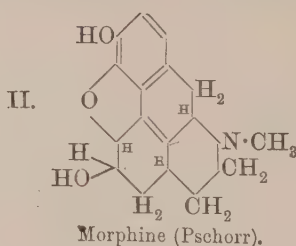
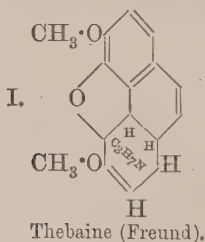
⁵ *Bull. Soc. chim.*, 1906, [iii], **35**, 1 ; *Arch. Pharm.*, **244**, 375.

⁶ *Ber.*, 1906, **39**, 2239.



the conversion of thebaine into codeinone elucidating the relationships of the two latter substances. This conversion has been effected in two different ways; Freund¹ obtained an additive product of thebaine with bromine, but this could not be isolated on account of its spontaneous decomposition into methyl bromide and bromocodeinone, a substance which successively furnishes codeinone and codeine on reduction. L. Knorr and H. Hörlein² have, moreover, obtained small quantities of codeinone by the hydrolysis of thebaine with *N*-sulphuric acid.

The position of the ring containing nitrogen is still undecided, Freund is inclined to make it part of a bridged ring,³ whilst Pschorr has proposed a "piperidine" formula,⁴ which would receive support if his formula for *apomorphine*⁵ were correct. This last, however, necessitates a formula (IV) for methylmorphimethine which is incompatible with the results obtained for hydroxycodine by Knorr and Hörlein,⁶ the latter substance being capable of further transfor-



mation to hydroxymethylmorphimethine. Hydroxycodine differs from codeine in containing a hydroxyl group in place of hydrogen

¹ *Ber.*, 1906, **39**, 844.

³ *Ibid.*, 1905, **38**, 3234; 1906, **39**, 844.

⁵ *Ibid.* 1906, **39**, 3124.

² *Ibid.*, 1409,

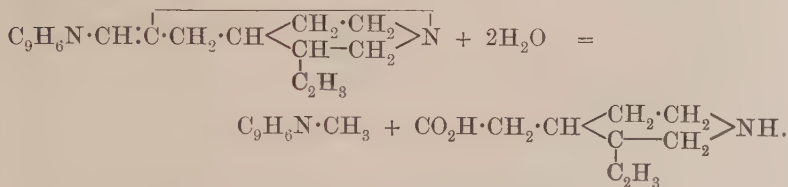
⁴ *Ibid.*, 1902, **35**, 4382.

⁶ *Ibid.*, 3252

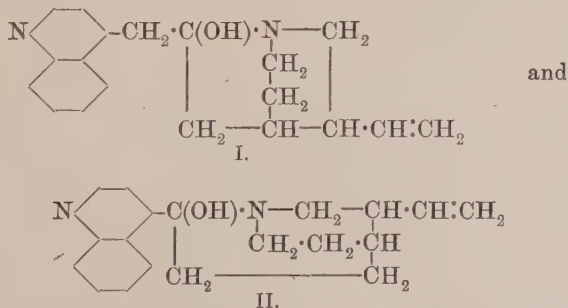
attached to one of the carbon atoms (9 or 10) of the bridge in the phenanthrene nucleus. This hydroxyl is alcoholic and not phenolic in function so that Freund's formula for thebaine is disproved, whilst formula IV for methylmorphimethine, necessitated by Pschorr's morphine formula, is also rendered untenable.

Knorr and Hörlein's most recent work deals with the transformation of chlorocodide into *pseudocodeine*¹ and the preparation of a fifth methylmorphimethine.²

Two very important papers on the cinchona alkaloids have appeared; in the first of these W. Koenigs³ gives a complete account of the work which has been carried out on these substances and then discusses the constitution of the non-quinolinic half of the molecule. The constitution of meroquinine, the product of the hydrolysis of cinchene, is definitely settled, so that the hydrolysis of cinchene to meroquinine and lepidine may be represented in the following manner:



The derivation of cinchene from cinchonine seems to have only two formulæ for cinchonine possible,



and of these, Koenig's proposed the first in 1900⁴ and has retained it in the present paper.

P. Rabe⁵ points out, however, that the latter formula agrees better with the properties of cinchotoxine—an isomerisation pro-

¹ *Ber.*, 1906, **39**, 4409.

² *Ibid.*, 4412.

³ *Annalen*, 1906 **347**, 143.

⁴ *J. pr. Chem.*, 1900, [ii], **61**, 1.

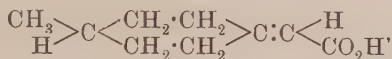
⁵ *Annalen*, 1906, **350**, 180.

duct of cinchonine. Cinchotoxine furnishes an *isonitroso*-derivative indicating that the grouping $\cdot\text{CH}_2\cdot\overset{|}{\text{C}}(\text{OH})\cdot\text{N}<$ in cinchonine becomes transformed into $\cdot\text{CH}_2\cdot\text{CO}\cdot$ and $\cdot\text{NH}\cdot$. Further, when this *isonitroso*-derivative is submitted to the Beckmann reaction the molecule breaks up, furnishing the nitrile of meroquinine and cinchoninic acid as products of fission. From this result Rabe decides that the second formula is to be preferred.

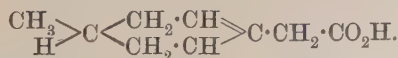
J. T. HEWITT.

STEREOCHEMISTRY.

ALL substances exhibiting optical activity in solution which have hitherto been prepared are known to contain one or more asymmetric atoms and it is customary to attribute the optical activity to the presence in the molecule of the asymmetric atom. It has, however, gradually become realised that the optical activity is a direct result of the enantiomorphous configuration of the molecule and that the latter is determined by the presence of the asymmetric atom ; it is possible to write numerous constitutional formulæ in which asymmetry is not associated with any component atom but which, interpreted in accordance with the tetrahedral configuration of methane, actually represent enantiomorphous molecular configurations. Thus, in the acid of the following constitution,



it must be supposed that the bonds in the hexamethylene ring all lie in one plane, that of the paper, and that the bonds attaching the groups H and CO₂H to that ethylenic carbon atom not in the ring also lie in the same plane. The bonds holding the H and CH₃ groups to the carbon atom in the para-position to the ethylene group must, however, lie in a plane at right angles to the first and therefore perpendicular to the paper and consequently the configuration represented must be an enantiomorphous one. No case of this kind was known until the present year, when W. Marckwald and R. Meth prepared an acid to which they assign the above constitution and resolved it into its optically active components by crystallisation with cinchonine ; they thus obtained the *dl*-4-methylcyclohexylidene-1-acetic acid with a specific rotatory power of $[\alpha]_D + 16^\circ$.¹ Subsequent to this, W. H. Perkin, jun., and W. J. Pope² state that they have prepared an acid to which they assign the above constitution and have been for some time endeavouring to resolve it ; their acid is different from that of Marckwald and Meth, and for the latter they suggest the following constitution :



¹ *Ber.*, 1906, **39**, 1171 and 2404.

² *Proc.*, 1906, **22**, 107.

Marckwald and Meth quote reasons¹ supporting the constitution which they originally assigned to their acid, and conclude that the acid of Perkin and Pope is the one which contains the double bond in the closed ring. In the event of Marckwald and Meth's view proving correct, their results must be regarded as marking a distinct advance in stereochemistry, in that they furnish the first case of a substance possessing optical activity in consequence of enantiomorphous molecular configuration not due to the presence of an asymmetric atom.

E. Erlenmeyer has continued his previous work² on the stereoisomeric cinnamic acids, $C_6H_5 \cdot CH:CH \cdot CO_2H$, and finds³ that from alcoholic solution three different brucine salts of synthetic cinnamic acid can be separated; these melt at 135° , 113° , and 107° respectively. Cinnamic acid from storax is less soluble in alcohol than the former and gives only the brucine salt melting at 135° ; this salt is practically inactive whilst the others are strongly lævorotatory in alcoholic solution. Erlenmeyer therefore suggests that cinnamic acid from storax is only one of the components of synthetic cinnamic acid, and supports this contention by quoting results obtained by crystallising cinnamic acid from the two sources with *d*- and *l*-isodiphenyloxyethylamine. The further investigation of these substances and their crystallographic examination has led Erlenmeyer and Barkow⁴ to conclude that the following six isomeric cinnamic acids must be regarded as distinct substances: (1) Erlenmeyer, sen.'s, *isocinnamic* acid, m. p. $37-38^\circ$; (2) *allocinnamic* acid, m. p. 68° ; (3) Liebermann's *isocinnamic* acid, m. p. 59° ; (4) anorthic cinnamic acid, m. p. 80° ; (5) α -cinnamic acid, m. p. $134-135^\circ$; (6) β -cinnamic acid, m. p. $132-133^\circ$. The *isocinnamic* acid contained in the most soluble of the brucine salts, which differs slightly in crystalline form from Liebermann's acid, and the synthetic acid apparently constitute two more isomerides. Erlenmeyer's conclusions have been criticised very adversely by W. Marckwald and R. Meth;⁵ these authors show that the salt melting at 113° contains alcohol of crystallisation and that the salt melting at 135° contains two molecules of cinnamic acid to each one of brucine. They also point out that on dissolving equivalent quantities of synthetic and natural cinnamic acid and brucine in alcohol, the solutions have the same rotatory power. They therefore conclude that the experimental evidence does not justify the conclusions of Erlenmeyer.

The view that mineral oil originates from the bacterial decomposition of proteins is put forward by C. Neuberg⁶ and supported by the

¹ *Ber.*, 1906, **39**, 2035.

³ *Ber.*, 1906, **39**, 285.

⁵ *Ibid.*, 1907, 1906, and 2598.

² *Ann. Report*, 1905, 168.

⁴ *Ibid.*, 1570.

⁶ *Biochem. Zeit.*, 1906, **1**, 368.

similarities between the optically active acids of petroleum and those obtained by the putrefaction of cheese, gelatin, &c. Vegetable lipase was found to liberate *d*-dibromostearic acid and a dextrorotatory glyceride from *dl*-dibromostearic triglyceride, showing that unorganised ferments are capable of producing optically active substances from inactive fats.

E. Fischer¹ has contributed in the connected form of a lecture a valuable digest of his chemical investigation of the amino-acids, polypeptides, and proteins, in which the stereochemical relations of these substances are fully considered.

α -Bromoisohexoic acid has been resolved into its optically active components by E. Fischer and H. Carl,² the method employed being the crystallisation of the mixed brucine salts; the levorotatory acid yields *d*-leucine ($[\alpha]_D - 14.20^\circ$) with ammonia. α -Bromo- β -phenylpropionic acid, $C_6H_5 \cdot CH_2 \cdot CHBr \cdot CO_2H$, has also been resolved by crystallisation with brucine and quinine; the levorotatory acid gives *d*-phenylalanine, $C_6H_5 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, ($[\alpha]_D + 31.78^\circ$) with ammonia. Fischer also describes convenient methods³ for preparing *d*- and *l*-leucines, and for converting these amino-acids into derivatives of *d*- α -bromoisohexoic acid. He has resolved⁴ synthetic α -aminoisovaleric acid into its optically active components by crystallising its formyl derivative with brucine; the compound of the *l*-acid crystallises as the less soluble product. Fischer gives the name valine to the acid and identifies *d*-valine with the active aminovaleric acid, $(CH_3)_2CH \cdot CH(NH_2) \cdot CO_2H$, separated from lupins, horn, and casein; *d*-valine has a bitter taste, whilst the *l*-isomeride, which has not yet been found in nature, possesses a pronounced sweet flavour. This distinction between the taste of two enantiomorphously related isomerides is similar to that observed in the case of the leucines and asparagines.

E. Fischer and W. A. Jacobs⁵ have resolved externally compensated *p*-nitrobenzoyl-*dl*-serine, $OH \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, by crystallisation with quinine; the salt of the *d*-acid separates first and the *l*-acid remaining in the mother liquors is conveniently purified by crystallisation with brucine. The *d*- and *l*-serine,



prepared by hydrolysing the nitrobenzoyl derivatives, differ in taste, the former being the sweeter; the *l*-serine is identical with the serine isolated from silk. *iso*Serine, $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CO_2H$, and diamino-propionic acid have been also resolved by crystallising their benzoyl derivatives with optically active bases.

C. Neuberg and E. Ascher⁶ resolve $\alpha\beta$ -diaminopropionic acid,

¹ *Ber.*, 1906, 39, 530.

² *Ibid.*, 3996.

³ *Ibid.*, 2893.

⁴ *Ibid.*, 2320.

⁵ *Ibid.*, 2942.

⁶ *Biochem. Zeit.*, 1906, 1, 380.

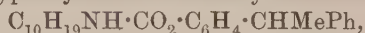
$\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, by crystallisation with *d*-camphorsulphonic acid; the salt of a *d*-rotatory acid is thus first separated but, as it is convertible into *l*-glyceric acid by the action of nitrous acid, it must be termed *l*- $\alpha\beta$ -diaminopropionic acid.

An improvement of Warburg and Fischer's method¹ of resolving α -bromopropionic acid, $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$, has been devised by L. Ramberg;² the *dl*-acid is frozen out from the acid which has been partially resolved by crystallisation with cinchonine.

dl-Aminobenzylidene- β -naphthol has been resolved by M. Betti³ by crystallisation with *d*-tartaric acid; the salt, *dBdA*, separates in almost theoretical yield as the more sparingly soluble salt.

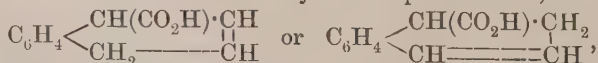
J. C. Irvine⁴ contributes a simple method for the separation of *l*-lactic acid from the *dl*-acid by crystallisation with morphine; morphine *l*-lactate crystallises readily from the mixed solution, and from the mother liquor the *d*-isomeride can be conveniently separated as the zinc salt.

R. H. Pickard and W. O. Littlebury⁵ use *l*-menthylcarbamide for the purpose of resolving externally compensated hydroxy-compounds into their optically active components; the method can be applied either by directly combining the carbimide and the hydroxy-compound, or by first converting the latter into a chlorocarbonic ester and then condensing with *l*-menthylamine. On applying the method to *dl*- α -phenyl- α' -4-hydroxyphenylethane, $p\text{-HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMePh}$, *d*- α -phenyl- α' -4-hydroxyphenylethane *l*-menthylcarbamate,



is obtained as the less soluble product and, on hydrolysis with soda, yields the optically active hydroxy-compound.

R. H. Pickard and J. Yates⁶ have resolved tetrahydro-1-naphthoic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} \text{CH}_2$, ($[\text{M}]_{\text{D}} 21.1^\circ$), and tetrahydro-2-naphthoic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, ($[\text{M}]_{\text{D}} 90.5^\circ$) into their optically active components by crystallisation with *l*-menthylamine; in each case the salt *lBIA* separates as the least soluble component. The molecular rotatory powers of the acid ions, stated in brackets above, are much smaller than that of the Δ^2 (or Δ^3)-dihydro-1-naphthoic acid,



namely, $[\text{M}]_{\text{D}} 374.5^\circ$, found by Pickard and Neville.⁷

R. H. Pickard and W. O. Littlebury⁸ have resolved *ac*-tetrahydro-

¹ *Ann. Report*, 1905, 174.

³ *Gazzetta*, 1906, 36, ii, 392.

⁵ *Ibid.*, 467.

⁷ *Ibid.*, 1905, 87, 1766.

² *Annalen*, 1906, 349, 324.

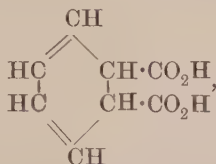
⁴ *Trans.*, 1906, 89, 935.

⁶ *Ibid.*, 1101.

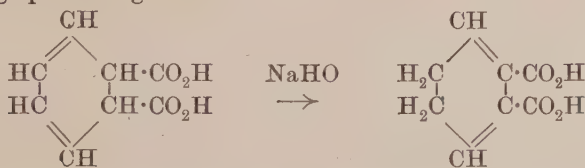
⁸ *Ibid.*, 1906, 89, 1252.

2-naphthol, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagdown \quad \diagup \\ CH_2 \cdot CH \cdot OH \end{smallmatrix}$, by their method which involves condensation with *l*-menthylcarbamide and crystallisation of the resulting mixture of the products *lBdA* and *lBLA*; in the present case the former compound proves to be the less soluble and is readily hydrolysed, yielding the *d-ac*-tetrahydro-2-naphthol. This substance does not readily undergo optical inversion, and therefore contrasts in behaviour with the corresponding amine which Pope and Harvey¹ found to be very easily inverted.

$\Delta^{2:4}$ -Dihydrophthalic acid was resolved into its active components by Proost² by crystallisation with strychnine, and A. Neville³ has now resolved the isomeric *trans*- $\Delta^{3:5}$ -compound,



by crystallisation of its acid strychnine salt. The salt of the *l*-base with the *l*-acid separates from the solution as the least soluble component. The cold aqueous solution of the *l*- $\Delta^{3:5}$ -dihydrophthalic acid does not undergo optical inversion in the cold, but at 97° the inversion of the sodium salt proceeds as a unimolecular reaction; the transformation occurs, also as a unimolecular reaction, much more rapidly in presence of excess of soda. From the solution remaining after the transformation the optically inactive $\Delta^{2:6}$ -dihydrophthalic acid has been isolated, the change proceeding thus:



A. Neville⁴ has also resolved the 2:3-dihydro-3-methylindene-2-carboxylic acid, $C_6H_4 \begin{smallmatrix} CHMe \\ \diagdown \quad \diagup \\ CH_2 \end{smallmatrix} \cdot CH \cdot CO_2H$, into its optically active components by crystallisation with *l*-menthylamine; the salt *lBdA* is the most sparingly soluble, and from this the pure *d*-acid is obtained. Although the acid contains two asymmetric carbon atoms only one *d*- and *l*-acid were isolated.

F. W. Kay and W. H. Perkin, jun.,⁵ have resolved synthetic *dl*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid,

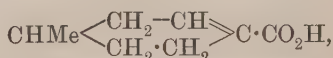
¹ *Trans.*, 1901, **79**, 83.

² *Ber.*, 1894, **27**, 3185.

³ *Trans.*, 1906, **89**, 1744.

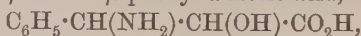
⁴ *Ibid.*, 383.

⁵ *Ibid.*, 839.



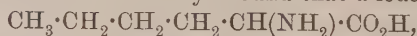
by crystallisation with brucine and strychnine; with the first base the salt *lBIA* is obtained as the less soluble, whilst with strychnine the salt *lBdA* crystallises first. From these acids, by the aid of the Grignard reaction, the authors have succeeded in obtaining for the first time synthetic optically active terpenes and their derivatives.

E. Erlenmeyer⁵ has resolved *dl*- α -bromo- β -phenyl- β -lactic acid, $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$, into its optically components by crystallisation with cinchonine and strychnine; the corresponding chloro-derivative has been resolved by means of strychnine and the iodo-derivative with the aid of cinchonine. E. Erlenmeyer and C. Barkow have prepared a *dl*- β -amino- β -phenyl- α -lactic acid,



isomeric with that already known, by the action of ammonia on sodium phenyl-lactate; the *laevo*-acid is prepared from sodium phenyl-lactate.

E. Abderhalden and F. Samuely² found that *d*-leucine,



is excreted in the urine after administering externally compensated leucine to rabbits; leucine is in general not excreted in the urine of dogs, although in one case the administration of the inactive amino-acid resulted in a small quantity of *d*-leucine being found in the urine.

On administering externally compensated alanine to dogs, A. Schittenhelm and A. Katzenstein find³ that only *l*-alanine is excreted the amino-acid is conveniently separated by aid of its α -naphthalene-sulphonic derivative.

O. Warburg⁴ shows that pancreatin hydrolyses leucine ethyl ester asymmetrically, *l*-leucine, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$, being produced.

F. Ehrlich⁵ finds that by the action of yeast on a solution of sucrose and externally compensated alanine, leucine, or α -aminoisovaleric acid, both components of the amino-acid are attacked, but, in general, at very different rates; *l*-alanine, *d*-leucine, or *l*- α -aminoisovaleric acid can be readily separated from the product in a 65 to 75 per cent. yield.

According to E. Reiss,⁶ *d*-alanine is more readily utilised in the animal organism than is its enantiomorphously related isomeride.

P. Mayer⁷ finds that *d*-lecithin is converted into *dl*-lecithin by heating to 100° with methyl alcohol, and that steapsin attacks

¹ *Ber.*, 1906, **39**, 788.

² *Zeit. physiol. Chem.*, 1906, **47**, 346.

³ *Zeit. exp. Path. Ther.*, **2**, 560.

⁴ *Zeit. physiol. Chem.*, 1906, **48**, 205.

⁵ *Biochem. Zeit.*, 1906, **1**, 8; *Zeit. Ver. deut. Zuckerind.*, 1906, No. **608**, 840.

⁶ *Beitr. chem. Physiol. Path.*, 1906, **8**, 332.

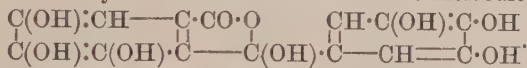
⁷ *Biochem. Zeit.*, 1906, **1**, 39.

dl-lecithin, leaving *l*-lecithin in the solution. O. Riesser¹ shows that *d*-arginine is converted into a mixture of *dl*-arginine and *dl*-ornithine by heating with diluted sulphuric acid at 160—180°.

A number of optically active alkyl derivatives of benzene have been prepared by A. Klages and R. Sautter.² The fact that these hydrocarbons are formed without optical inversion from their sulphonic acids has led Klages³ to attempt the resolution of *sec*-butylbenzene, CHMeEtPh, by crystallising the sulphonic acid of the externally compensated hydrocarbon with quinine, cinchonidine, and strychnine; the attempts were not successful.

Pschorr, Roth, and Tannhäuser⁴ show that the optically active α - and β -methylmorphimethines and α -ethylthiocodide crystallise in the sphenoidally hemihedral subdivision of the orthorhombic system and afford examples of the recently discovered occurrence of optical activity⁵ in the crystalline state of biaxial substances.

In view of the optical activity and other properties of tannin, J. Dekker⁶ assigns to it the following constitution which indicates the presence of an asymmetric carbon atom in the molecule,



Haller and March⁷ have prepared, and determined the specific rotatory powers of, hexahydrobenzyl-, hexahydrobenzylidene-, oenanthyl-, and oenanthylidene-camphors; the results confirm the previous conclusion that the specific rotatory power of the unsaturated derivative is higher than that of the corresponding saturated compound.

The statement is made by E. Jungfleisch and M. Godchot⁸ that during the preparation of *d*- or *l*-lactide by heating the corresponding lactic acid, they observe that *l*-lactic acid or *l*-lactide is much more rapidly optically inverted by heat than the corresponding *d*-isomeride.

In continuation of previous work, J. B. Cohen and I. H. Zortmann have prepared, and determined the rotation constants of, the *l*-menthyl esters of the isomeric dibromobenzoic acids,⁹ and J. B. Cohen and H. P. Armes have prepared and examined the *l*-menthyl esters of the isomeric chloronitrobenzoic¹⁰ and dinitrobenzoic¹¹ acids.

R. H. Pickard and J. Yates¹² have examined as a time reaction the conversion of the sodium or methyl salts of *d*- Δ^2 -dihydro-1-

¹ *Zeit. physiol. Chem.*, 1906, **49**, 210.

² *Ber.*, 1906, **39**, 1938; compare *Ann. Report*, 1905, 178.

³ *Ber.*, 1906, **39**, 2131. ⁴ *Ibid.*, 19. ⁵ Pocklington, *Phil. Mag.*, 1900, **6**, 2.

⁶ *Ber.*, 1906, **39**, 2497 and 3784. ⁷ *Compt. rend.*, 1906, **142**, 316.

⁸ *Ibid.*, 637.

⁹ *Trans.*, 1906, **89**, 47.

¹⁰ *Ibid.*, 454.

¹¹ *Ibid.*, 1479.

¹² *Ibid.*, 1484.

naphthoic acid into the inactive Δ^1 -acid, $\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{CO}_2\text{H})\cdot\text{CH} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$, in presence of a number of basic hydroxides and bases; the conversion proceeds as a unimolecular reaction and is easily followed polarimetrically.¹ The hydroxides of the alkaline earths hasten the transformation of the sodium salt more than the alkali hydroxides, and the latter are rather more active than the tetra-alkylammonium hydroxides; the relative strengths of the bases in this respect differ somewhat from the relative electric conductivities, and this is attributed to the effect of the base on the electrolytic dissociation of the salt. R. H. Pickard, W. O. Littlebury, and A. Neville² have studied the reactions between *l*-menthylcarbimide and a number of alcohols as time reactions; the rotation constants of a number of esters of *l*-menthyl-carbamic acid have been determined.

Further examples of asymmetric syntheses are given by A. McKenzie,³ who applies Grignard's reaction for this purpose. The action of magnesium propyl, *isobutyl*, *tert.*butyl, and α -naphthyl iodides or bromides on *l*-menthyl benzoylformate and of magnesium methyl, ethyl, *iso*-butyl, and α -naphthyl iodides or bromides on *l*-bornyl benzoylformate leads in each case to an asymmetric synthesis of a substituted glycollic acid. In each case a mixture of the *d*- and *l*-substituted glycollic acids resulted on hydrolysis of the product, and in this mixture one component predominated; the excess of one component over the other was greater in the case of the menthyl than of the bornyl esters. The asymmetric synthesis of phenymethylglycollic acid can be effected both by the action of magnesium methyl iodide on *l*-menthyl benzoylformate and by that of magnesium phenyl bromide on *l*-menthyl pyruvate; the former method leads to formation of excess of the *l*-acid, whilst the latter gives the *d*-acid in larger quantity. A. McKenzie and H. Wren⁴ also effect an asymmetric synthesis of *l*-lactic acid by the reduction of *l*-bornyl pyruvate and subsequent hydrolysis of the product.⁵

W. Marckwald and D. M. Paul⁶ have shown that on heating either *dl*- or *l*-mandelic acid, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, with the equivalent quantity of brucine at 150—160° it becomes converted into *d*-mandelic acid, that is to say, the mandelic acid subsequently separated shows a slight dextrorotation. Similarly, on heating *dl*-mandelic acid with strychnine or nicotine under the same conditions, the recovered acid is dextrorotatory. On heating *dl-p*-methoxymandelic acid with brucine or strychnine, it becomes dextrorotatory, and

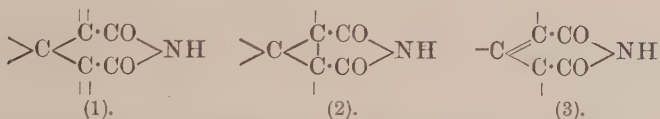
¹ *Ann. Report*, 1905, 174.² *Trans.*, 1906, 89, 93.³ *Ibid.*, 365.⁴ *Ibid.*, 688.⁵ Compare *Ann. Report*, 1905, 170.⁶ *Ber.*, 1906, 39, 3654.

after heating β -phenyl-lactic acid with brucine the recovered acid is found to be slightly laevorotatory.

Winther shows¹ that in the catalytic optical inversion of *d*-tartaric acid, *i*-tartaric acid is first produced, the reaction being one of the first order and reversible; the generally accepted view that the *dl*-tartaric acid produced during the optical inversion of *d*-tartaric acid is a direct product of the change is thus incorrect. The *dl*-tartaric acid obtained is produced from *d*-tartaric acid, *i*-tartaric acid being formed as an intermediate product. The effect of alkalis in accelerating the optical inversion of *d*-tartaric acid is connected with the presence of hydroxylic hydrogen, which becomes replaced by the alkali metal; thus the substance $\text{CO}_2\text{Na}\cdot\text{CH}(\text{ONa})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Na}$ can be separated from strongly alkaline solutions of sodium tartrate and caustic soda. No corresponding compound containing potassium could be isolated and in accordance with this it is observed that caustic potash exercises a slighter catalytic effect on the inversion than soda. He has also found² that the optical inversion of mandelic acid by caustic alkalis proceeds as a unimolecular reaction.

J. Mauthner³ finds that β -cholestene dibromide gives $[\alpha]_D - 39.6^\circ$ immediately after solution in chloroform but that the solution becomes optically inactive in a day and after several days gives the specific rotatory power $[\alpha]_D + 39.4^\circ$; the change occurs more slowly in benzene solution and the solution on evaporation yields the isomeric α -cholestene dibromide.

R. Torrese⁴ has shown that the hydrolysis of sucrose is not brought about by glutaconimide derivatives of types (1) and (2), but that those derivatives which contain the group (3)



are alone capable of causing the hydrolysis. The presence of the single double linking in (3) is thus essential if the derivative is to bring about the hydrolysis of sucrose; further, if one of the carbonyl groups is replaced by the group CMe_2 , the power to hydrolyse sucrose is lost.

A convenient method for graphically representing the configurations of sugar-like substances and their derivatives is given by Rosanoff⁵; he considers that the stereochemical classification of these and related substances would be rendered more consistent by regarding *d*-gulose

¹ *Zeit. physikal. Chem.*, 1906, **56**, 719.

² *Ibid.*, 465.

³ *Monatsh.*, 1906, **27**, 421.

⁴ *Atti R. Accad. Sci. Torino*, 1906, **41**, 309.

⁵ *J. Amer. Chem. Soc.*, 1906, **28**, 114.

as belonging to the *l*-family and not to that of *d*-glucose and by making corresponding changes in the nomenclature of other similarly related compounds. He also discusses¹ the question of optical superposition and states as a new principle that "the optical rotatory power of an asymmetric carbon atom depends upon the composition, constitution, and configuration of each of the four groups."

T. M. Lowry² has applied his solubility method³ for determining the proportions in which dynamic isomerides are in equilibrium in solution, to the halogen derivatives of camphor which Kipping has shown to undergo reversible isomeric change in presence of alkalis. He finds that the solubility of each of these substances which contains the group $\text{-CHBr}\cdot\text{CO-}$ or $\text{-CHCl}\cdot\text{CO-}$ is increased by approximately one-tenth by the addition of the alkali, but no such increased solubility is observed with camphor derivatives containing the group $\text{-CH}_2\cdot\text{CO-}$ or $\text{-CBr(NO}_2)\cdot\text{CO-}$. The extent to which the partial optical inversion occurs is a result of the isodynamic reversal in sign of the asymmetric carbon atom in the group $\text{-CHBr}\cdot\text{CO-}$ or $\text{-CHCl}\cdot\text{CO-}$. T. M. Lowry and E. H. Magson⁴ have applied similar methods to the study of a large number of sulphonic derivatives of camphor, and have obtained evidence enabling the above conclusions to be extended.

T. Purdie and C. R. Young⁵ regard ordinary crystalline rhamnose as the α -form and Fischer's crystalline anhydrous rhamnose as the β -form of the sugar; they describe an improved method for the preparation of the latter form, which involves assisting the change $\alpha \rightarrow \beta$ to occur. The β -rhamnose is stable at high temperatures and the α -form at low temperatures; the former is *l*-rotatory and the latter strongly *d*-rotatory in aqueous solution. A number of methyl-rhamnosides have been prepared and classified as of the α - and β -form.

T. Purdie and R. E. Rose⁶ have isolated β -methylarabinoside corresponding to Fischer's α -methylarabinoside from the mother liquors obtained during the preparation of the latter; both are unaffected by yeast enzymes or by emulsin. Trimethyl- α -arabinoside is crystalline and was isolated; the β -isomeride is apparently a liquid and has a lower dextrorotation than the former.

J. C. Irvine and A. M. Moodie⁷ have investigated the addition of alkyl iodides to alkylated sugars and glucosides, and, from the behaviour of tetramethyl- α - and - β -glucosides and tetramethyl glucose towards such substances, conclude that the observed mutarotation takes the following course when the solutions are cooled and then reheated: (1) a decrease in rotatory power owing to formation of an oxonium derivative; (2) an increase in rotatory power at the lower temperature owing to the

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 524.

² *Ibid.*, 1904, **85**, 1541.

³ *Ibid.*, 1194.

⁴ *Trans.*, 1906, **89**, 1033.

⁵ *Ibid.*, 1906, **89**, 1042.

⁶ *Ibid.*, 1204.

⁷ *Ibid.*, 1578.

uncombined sugar changing in the direction $\beta \rightarrow \alpha$; (3) a rapid rise in rotatory power during reheating owing to the dissociation of the oxonium derivative; and (4) a fall in rotatory power at the higher temperature due to the change $\alpha \rightarrow \beta$ in the sugar.

P. Walden¹ has determined the rotation constants of a large number of optically active esters and other substances for light of different wave-lengths under a variety of different conditions of solvent, concentration, and temperature. He concludes that the rotatory dispersion is a highly constitutive property, and is in the main independent of the temperature and solvent; homologous substances have practically the same rotatory dispersions, "but deviations from this rule are found in the lower members of a homologous series. A high rotatory power usually accompanies a high rotatory dispersion, although this is not always true, the two constants being not generically related. Most solvents have little influence on the rotatory dispersion of a dissolved substance, but some, which differ widely in constitution and optical properties, exert a distinct influence on the rotatory dispersion of the solute. A few solvents, such as chloroform, quinoline, and cinnamaldehyde, sometimes effect a complete change in the rotatory dispersion of the solute; this alteration is to be traced to chemical change leading to the formation of new optically active complexes. Walden replies² to Patterson's criticism of his previous conclusions,³ quoting a large amount of fresh experimental data, and adhering to his former statement that a direct relation is observable between the molecular weight and the rotatory power of an optically active substance in both concentrated and dilute solutions.

C. Winther⁴ contributes a quantity of experimental data from which he concludes that a simple relation exists between changes of rotatory power on the one hand and the specific volume and molecular weight on the other. In the case of certain substances, such as nicotine and amyl itaconate, the results obtained at different temperatures indicate that the changes in rotatory power are due solely to changes in the molecular volume or molecular solution volume; the same holds in numerous cases investigated by Frankland and Patterson, in which the rotatory power and molecular volume change proportionally when the temperature is altered. In other cases, such as those of menthol, ethyl and propyl tartrates, and diethyl dibenzoyltartrate, the changes of rotatory power are functions of the changes in molecular volume and also in molecular weight. If a certain change in rotatory power, $\Delta[\alpha]$, occurs as the result of the quantity, Δm_1 , of single molecules being produced from double

¹ *Zeit. physikal. Chem.*, 1906, **55**, 1.

² *Ber.*, 1906, **39**, 658.

³ *Ann. Report*, 1905, 176.

⁴ *Zeit. physikal. Chem.*, 1906, **55**, 257; **56**, 703.

molecules in the liquid by a rise of temperature, T , the change in rotatory power should be represented by

$$\Delta[\alpha] = K \cdot \Delta m_1 + K_2 \cdot \Delta v = K_1 \cdot \Delta T / T T_1 + K_2 \cdot \Delta v.$$

This expression applies satisfactorily to the substances last mentioned both in the undissolved and dissolved state. The amount of association occurring in the solutions may be determined from a knowledge of the changes in rotatory power and in molecular volume, because $K \cdot \Delta m_1 = \Delta[\alpha] - K_2 \cdot \Delta v$.

Cases like those of nicotine and ethyl tartrate, in which $\Delta[\alpha] = K \cdot \Delta v$, are found in camphor and turpentine in the dissolved state.

Grossmann and Wieneke¹ from an extensive series of rotatory power determinations at different temperatures and concentrations conclude that in aqueous solution boric acid and tartaric acid form a monoboryltartaric acid, $\text{CO}_2\text{H} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2 \cdot \text{BO}$, the hydrolytic dissociation of which increases with rise of temperature and decrease of concentration. The sodium salt of this acid appears to exist in solution and evidence of the formation of a sodium boryl bitartrate is also adduced. Both normal and acid tartrates and malates of pyridine exist in aqueous solution.

With the aid of the approximately monochromatic light of wave-length 488.5μ which passes through a pale-blue light filter, H. Grossmann² has investigated the optical effect of adding alkaline copper solutions to solutions of *d*-glucose, *d*-fructose, *d*-mannitol, *d*-rhamnose, sucrose, isosaccharin, asparagine, and tartaric and quinic acids. The effect of the alkaline copper solution is in all cases greatly to increase the rotatory power, and in the cases of glucose, fructose, sucrose, and rhamnose, the sign of the rotation is reversed. The maximum changes in specific rotatory power due to the addition of copper solution are from $+78.0^\circ$ to -375° with glucose, -134.5° to $+1423^\circ$ with fructose, $+101.2^\circ$ to -111.3° with sucrose, and $+72.0^\circ$ to $+1327^\circ$ with tartaric acid.

T. S. Patterson and J. Kaye³ have examined *l*-menthyl *l*-tartrate for purposes of comparison with *l*-menthyl *d*-tartrate.⁴ *l*-Menthyl *l*-tartrate gives $[\text{M}]_D -358.1^\circ$ at 15° and -382.5° at 103° in the pure state and, together with its diacetyl derivative, has been examined in a number of solvents. It is shown that the optical effect of each component optically active group in the two diacetyl derivatives is roughly traceable in the changes of molecular rotatory power which occur on heating from 0° to 100° and the results are discussed in connexion with the question of optical superposition.

T. S. Patterson and J. Frew⁵ have determined the rotatory powers

¹ *Zeit. physikal. Chem.*, 1906, **54**, 385.

² *Zeit. Ver. deut. Zuckerind.*, 1906, No. **610**, 1024.

⁴ *Ann. Report*, 1905, 176.

³ *Trans.*, 1906, **89**, 1884.

⁵ *Trans.*, 1906, **89**, 332.

of *l*-menthyl benzenesulphonate and β -naphthalenesulphonate in alcohol, benzene, and nitrobenzene solutions at different temperatures and concentrations; the values for the benzenesulphonate are larger than those for the other ester, and in each case the highest values are obtained in alcohol solutions, the lowest in nitrobenzene, and intermediate values in benzene solutions.

In addition to those previously described,¹ P. F. Frankland and D. F. Twiss² have determined the rotatory powers of a number of other derivatives of tartramide; it is notable that the specific rotatory power of *d*-tartaric diallylamide is less than that of the dipropylamide, as this forms an exception to the general rule that the introduction of a double bond increases the specific rotatory power. A similar observation is made by P. F. Frankland and E. Done³ in an investigation on the influence of substituents on the optical activity of malamide; it is there shown that maldi-*n*-propylamide has a higher specific rotatory power than maldiallylamide.

The autoracemisation of iodides and bromides of optically active quarternary ammonium bases in chloroform solution first observed in the case of phenylbenzylmethylallylammonium compounds and the optical stability in aqueous solution of the corresponding salts of the same base in aqueous solution⁴ have been reinvestigated by Wedekind⁵ in connexion with the iodide, bromide, chloride, and fluoride of *d*-phenylbenzylmethylpropylammonium. As in the first-mentioned case, the iodide undergoes autoracemisation in chloroform solution more rapidly than the bromide; with the fluoride no definite indication of autoracemisation was obtained and the hydroxide in chloroform solution becomes slowly optically inverted, although Wedekind has previously noted that another optically active substituted ammonium hydroxide is optically stable in aqueous solution.

E. Wedekind⁶ finds that the optical inversion of phenylbenzylmethyl-, allyl-, -propyl- and -isobutyl-ammonium iodides proceeds as a unimolecular reaction. The molecular weight of the first compound is normal, so that but very slight dissociation can exist in the chloroform solution. H. Goldschmidt⁷ does not consider it certain that Wedekind's measurements completely establish that the optical inversion is due to dissociation into tertiary amine and alkyl iodide; he contributes a thermodynamical discussion of the process of optical inversion.⁸

E. Wedekind and E. Fröhlich⁹ remark that the molecular rotatory powers previously given by Wedekind and Jones for the optically

¹ *Trans.*, 1903, **83**, 1349.

² *Ibid.*, 1906, **89**, 1855.

³ *Ibid.*, 1859.

⁴ *Trans.*, 1901, **79**, 828.

⁵ *Ber.*, 1906, **39**, 474.

⁶ *Zeit. Elektrochem.*, 1906, **12**, 330.

⁷ *Ibid.*, 416 and 516.

⁸ Compare Wedekind, *ibid.*, 1906, **12**, 515.

⁹ *Ber.*, 1906, **39**, 4437.

active ion $\cdot\text{NMeEtPh}\cdot\text{C}_7\text{H}_7$ are not such as would be expected from the values obtained for the ions



In accordance with this it was found that prolonged fractional crystallisation of the mixed *d*- and *l*-phenylbenzylmethylethylammonium *d*-camphorsulphonates led to the separation of a fraction, *dBdA*, having a much higher rotatory power than in the previous work and from which the value $[\text{M}]_{\text{D}} + 64.4^\circ$ was obtained for the basic ion. The iodide of the active base undergoes optical inversion rapidly in chloroform but not in alcohol solution.

Wedekind agrees with Jones's view¹ that the so-called β -phenylbenzylmethylallylammonium iodide is really phenylbenzyltrimethylammonium iodide, which is formed in the reaction between phenylbenzylallylamine and methyl iodide by a replacement of the allyl group by methyl; he describes several cases of a similar kind in which an allyl or benzyl group is thus displaced by methyl during the formation of a quaternary ammonium iodide. There is therefore at present no known case of stereoisomerism amongst optically inactive asymmetric nitrogen derivatives.²

Miss M. B. Thomas and H. O. Jones³ have determined for purposes of comparison the rotation constants at different temperatures and concentrations of a large number of compounds owing their activity to the presence of a asymmetric nitrogen atom; the interpretation in the light of Guye's formula of the large quantity of valuable data quoted led to no satisfactory agreement being established between the observed and the calculated values.

A. Ladenburg⁴ has continued work on the peculiar kind of stereochemical isomerism which he believes to occur amongst secondary bases like stilbazoline and coniine.⁵ Whilst the naturally occurring *d*-coniine has $[\alpha]_{\text{D}} + 15.6^\circ$, the base obtained by resolving synthetic coniine with *d*-tartaric acid gives $[\alpha]_{\text{D}} + 19.2^\circ$; the latter Ladenburg regards as *d*-isoconiine. The only difference observable between the properties of the two bases and their derivatives is in the specific rotatory power. *d*-isoConiine undergoes practically complete conversion into *d*-coniine of $[\alpha]_{\text{D}} + 15.7^\circ$ on heating at $290-300^\circ$.

W. J. POPE.

¹ *Ann. Report*, 1905, 182.

² *Ber.*, 1906, 39, 481.

³ *Trans.*, 1906, 89, 280.

⁴ *Ber.*, 1906, 39, 2486.

⁵ *Ann. Report*, 1904, 144.

ANALYTICAL CHEMISTRY.

THE problems of analytical chemistry cover such an exceedingly wide field, and are, if I may be permitted to use the expression, of such a heterogeneous character, that it is practically impossible to present this report in the form of a continuous and connected narrative. Advances of distinct significance often consist merely in the detection of some source of error in a more or less well known process and its elimination or in a slight modification of some existing piece of apparatus. Trivial as these matters may appear when compared with some of the discoveries made in other branches of our science, they are nevertheless often of prime importance to the analyst, and as such claim attention in this review. In place of the unbroken and more readable story which the author would have liked to present, he is, from the very nature of the subject, compelled to deal largely with disconnected and isolated facts, and he can only hope that in consequence of the arrangement of the subject matter which he has adopted he has been able to preserve in parts some semblance of sequence and continuity. The adoption of a definite plan is as necessary for the Reporter as for the Reader, and it is believed that the arrangement of the subject followed last year is that which lends itself most readily to clear and methodical treatment. The subjects referred to in this report will therefore be dealt with under the following headings :

1. Inorganic Chemistry including Electrochemical methods.
2. Organic Analysis.
3. Analysis of Foods and Drugs.
4. Toxicological Analysis.
5. Apparatus.

The arbitrary character of this or indeed of any other subdivision will be evident, and in some cases there is perhaps no good reason why a particular process should have been discussed under one heading rather than under some other. Still the method has certain practical advantages and appears to the author to answer its purpose well.

Inorganic Analysis.

It comparatively rarely happens that new reactions likely to be of real service in qualitative inorganic analysis are recorded, although

there is unquestionably a large field still open for investigation in this branch of analytical chemistry, more especially in connexion with the detection of some of the rarer elements and the easier identification of traces of one metal in the presence of large quantities of another from which it cannot be easily separated by existing methods. The importance of studying the metallic derivatives of organic compounds from this point of view is now thoroughly recognised, and observations are from time to time recorded which are usually interesting, if not always of practical utility. Bradley¹ finds that the hæmatoxylin reaction of copper, which has long been known, although but little used, is far more sensitive than that given by potassium ferrocyanide or even by starch and potassium iodide, and in the same paper points out that traces of zinc in tissue ashes containing relatively large quantities of copper, iron, calcium, and phosphoric acid may readily be detected by taking advantage of the fact that zinc nitroprusside differs from all the other insoluble nitroprussides in readily forming well defined crystals which can be recognised by means of the microscope. According to Grossmann and Schück² dicyanodiamide constitutes a fairly delicate test for nickel even in the presence of a large excess of cobalt, although its sensitiveness is evidently very much inferior to that of Tschugaëff's reagent referred to below.

For the detection of gold and platinum, more especially when present in small quantities in the presence of other metals, Petersen³ outlines a scheme which appears to be capable of useful application, although it does not embody any new principle. The solvent action of boiling sulphuric acid on platinum in the presence of ammonium sulphate has been made the subject of several papers by Delépine during the past few years, and in a recent communication⁴ he states that platinum-iridium alloys are appreciably soluble in strong sulphuric acid at a temperature of 365°, and that on boiling the resulting solution with ammonium sulphate the platinum is deposited, the iridium remaining in solution. This solution, which appears to contain ammonium iridium sulphate, exhibits the green colour becoming deep violet on the addition of nitric acid, which is a characteristic reaction of iridium. The colour is so intense that it is said to be possible by its means to detect iridium in many samples of commercial 'pure platinum.'

The detection of small quantities of yellow phosphorus in phosphorus trisulphide (and in match heads) has been made a subject of investigation by several chemists, and an interesting process has been devised for this purpose by Schenck and Scharff,⁵ depending on

¹ *Amer. J. Sci.*, 1906, [iv], 22, 326.

² *Zeit. anal. Chem.*, 1906, 45, 342.

³ *Ber.*, 1906, 39, 1522.

⁴ *Ber.*, 1906, 39, 3356.

⁵ *Compt. rend.*, 1906, 142, 631.

the increase in the rate of discharge of an electroscope when subjected to the action of air in which the sample containing phosphorus has been slowly oxidised. The method appears to be capable of being usefully employed in toxicological analysis, and might be useful for the purpose of controlling the purity of the air in rooms or factories in which phosphorus is used.

The detection of small quantities of nitric oxide and ozone in the presence of one another is not an easy problem, and F. Fischer and Marx¹ show that this may be done by leading the mixture into liquid air, which dissolves the ozone and solidifies the nitric oxide. After separation by filtration, the two substances may be identified by the employment of wet "tetramethyl-base paper" (4:4'-tetramethyldi-aminodiphenylmethane). The use of liquid air in this connexion is interesting.

The nitroprusside test for sulphides is not perhaps a very important one, but it is occasionally useful, and it is well that its limits of sensitiveness and the extent to which other acid radicles may interfere should be understood. Following Reichard, Virgili² has studied the reaction, and has found that the blue coloration, which is prevented by the presence of free alkali, is also very considerably interfered with by the presence of silicates, phosphates, borates, and other salts which are capable of yielding alkali on hydrolysis. It is, of course, well known that even under the most favourable conditions sodium nitroprusside constitutes a less sensitive reagent for sulphides than neutral or alkaline solutions of lead salts. This, according to the author, appears to be due to the fact that nitroprussides are not reagents for the sulphide ion, but for the non-ionised metallic salt, any condition which tends to prevent ionisation at the same time increasing the delicacy of the reaction.

In the quantitative section of this branch of analysis much good work has been done during the year. The electrical conductivity method has in several cases during recent years been successfully applied to the determination of the solubilities of very sparingly soluble substances, and, working in this way, Böttger³ finds that the solubilities of the chloride, thiocyanate, and bromide of silver in water at 100° are respectively 153×10^{-6} , 39×10^{-6} , and 20×10^{-6} gram-equivalents per litre. Every analyst knows from experience how great an error may be introduced into estimations involving the weighing of silver chloride if that substance is washed with unnecessarily large quantities of hot water, but it is well to realise that an aqueous solution of silver chloride saturated at 100° contains no less than 2.18 mg. per 100 c.c. In this connexion it is interesting to note that

¹ *Ber.*, 1906, **39**, 2555.

² *Zeit. anal. Chem.*, 1906, **45**, 409.

³ *Zeit. physikal. Chem.*, 1906, **56**, 83.

Donau¹ recommends the application of the conductivity method to the estimation of small quantities of gold and palladium in solutions reduced by means of carbon monoxide, and shows that even with exceedingly dilute solutions (0.0005 per cent.) the mean error is very small. Processes involving the employment of delicate electrical appliances are not as a rule well suited to the needs of the analytical chemist, but they appear to the author to be worthy of special notice, as indicating a praiseworthy tendency to press new methods into the service of analytical chemistry. For this reason the observation of Drapier,² that a galvanometer may be used as an "indicator" in the volumetric estimation of silver is noteworthy. The estimation of moisture in substances containing other constituents which volatilise on heating is a very common problem in the analytical laboratory and often one of serious difficulty. In a very interesting paper on this subject P. V. Dupré³ describes a method based on the interaction of the water and calcium carbide. The resulting acetylene is measured, and the process appears to be not only accurate, but capable of wide application. Thus it can be employed for the estimation of water in crystallised salts and of moisture in cordite and in mixtures containing volatile constituents such as camphor or naphthalene. There also appears to be some foundation for the hope that it may enable the analyst to distinguish between moisture and combined water. The use of the nephelometer for the estimation of opalescent silver chloride precipitates is dealt with by Wells⁴ and by Richards,⁵ both of whom indicate the chief precautions which must be observed in nephelometric work. Horn,⁶ and the same author and Sue. A. Blake,⁷ have made a detailed study of the question of sensitiveness in colorimetry, and have called attention to a fact which many analysts overlook, namely, that in every colorimetric process there is one dilution which gives the maximum degree of sensitiveness and consequently the most accurate analytical results. In their last communication the authors enunciate several generalisations in regard to colorimetric measurements which deserve the attention of analysts. The appearance of a further paper by Sørensen and Andersen⁸ on the selection of a substance for the standardisation of solutions employed in acidimetry goes to justify the use in my previous report of the word "perennial" as applied to this subject. The authors still advocate the use of sodium oxalate in opposition to Lunge, who prefers sodium carbonate, and deal with the important question of the choice of indicator. Acree and Brunel⁹ have also devoted attention to this subject, but their paper, although

¹ *Monatsh.*, 1906, **27**, 59.

³ *Analyst*, 1906, **31**, 213.

⁵ *Ibid.*, 510.

⁶ *Ibid.*, 253.

⁸ *Zeit. anal. Chem.*, 1906, **45**, 217.

² *Bull. Soc. chim. Belg.*, 1906, **20**, 148.

⁴ *Amer. Chem. J.*, 1906, **35**, 99 and 508.

⁷ *Ibid.*, 1906, **36**, 195 and 516.

⁹ *Amer. Chem. J.*, 1906, **36**, 117.

recording some useful observations, does not contain much that is really novel. A new indicator consisting of a condensation derivative of methylfurfuraldehyde which appears to possess useful properties is described by Fenton.¹ Several authors have dealt with the standardisation of solutions employed in iodimetric analysis and two papers—one by Bruhns² and the other by Riegler³ may be read with advantage. In the former the conditions necessary for obtaining accurate results when using potassium dichromate and iodide are discussed, and it is pointed out that potassium permanganate may be advantageously substituted for the dichromate. In the second paper Riegler advances claims on behalf of ammonium tri-iodate as a fundamental substance for use in iodimetry and in volumetric analysis generally. This substance which has the formula $(\text{NH}_4)_2\text{H}_2(\text{IO}_3)_3$ is crystalline, anhydrous, and non-hygroscopic, and is very stable both as a solid and in solution. Directions are given for using this salt in alkalimetric titrations and for ascertaining the strength of its solutions by means of hydrazine sulphate, with which it reacts with evolution of nitrogen, which can be measured. Mathewson and Calvin⁴ describe a method for estimating hydrogen peroxide by titration with a solution of ferrous ammonium sulphate or *vice versa*, the chief point of interest being the employment of a solution of titanium potassium sulphate as indicator, the peroxide giving with the titanium solution, as is well-known, a deep yellow coloration due to the formation of a higher oxide. In a preliminary communication Jannasch and Zimmermann⁵ describe a method for the quantitative separation of iodine from chlorine and bromine in which the mixture containing the three halogens is dissolved in a solution of hydrogen peroxide strongly acidified with acetic acid, and the liberated iodine distilled over with steam and collected in an ammoniacal solution of hydrazine sulphate. In a subsequent paper⁶ Jannasch deals with the separation of bromine and chlorine, and shows that from solutions acidified with sulphuric acid and containing hydrogen peroxide the former halogen may be distilled over in a current of carbon dioxide, leaving the chloride undecomposed. These separations, more particularly that of iodine, appear to be very complete, and the methods will no doubt be rigorously tested by chemists under the varying conditions of analytical practice. A further communication is promised by the same author on the application of the hydrogen peroxide method to the separation of the three halogens when present together and will be awaited with interest. According to Busch,⁷ nitrous acid can be quantitatively oxidised to nitric acid by hydrogen peroxide under certain conditions, and on this observation he has based a process for

¹ *Proc. Camb. Phil. Soc.*, 1906, **13**, 298.

² *Zeit. anorg. Chem.*, 1906, **49**, 277.

³ *Zeit. angew. Chem.*, 1906, **19**, 845.

⁴ *Amer. Chem. J.*, 1906, **36**, 113.

⁵ *Ber.*, 1906, **39**, 196.

⁶ *Ibid.*, 3655.

⁷ *Ibid.*, 1401.

the estimation of nitrite and nitrate when present together, the former being determined volumetrically by the permanganate method, and the total nitrate gravimetrically (after oxidation by hydrogen peroxide) by means of the "nitron" method, to which reference was made in my previous report.¹

Seyewetz and Bloch² find that when an aqueous solution of a hyposulphite is added to a solution of silver chloride in ammonia, reduction of the silver to the metallic state occurs quantitatively, and as sulphites, which are formed in the reaction, and thiosulphates, do not interfere, the method can be used with advantage for the estimation of hyposulphurous acid.

Manning and Lang³ have studied the question of the estimation of boric acid, alone and in the presence of phosphoric acid, and although the paper in which their results are recorded does not contain much that is new, it is deserving of the attention of analysts. The authors deal with the separation of the boric acid as the trimethyl ester, and its subsequent estimation either as the barium salt or by the ordinary method. Their results indicate that both processes are capable of being employed with a higher degree of accuracy than is usually supposed.

Methods for the detection and accurate estimation of traces of any of the elements are always welcome, especially in view of their importance in connexion with many of the problems of metallurgical and physiological chemistry, and in the last report on the progress of Analytical Chemistry⁴ I referred to the fact that Tschugaeff had suggested the employment of α -dimethylglyoxime as a delicate test for nickel. Armit and Harden⁵ have now applied this method to the quantitative estimation of very small quantities of nickel in animal tissues and other organic substances. The nickel having been separated by methods which are only slight modifications of those in common use, is estimated colorimetrically by means of Tschugaeff's reagent. The advantages of this method over that in which ammonium sulphide is employed are that the scarlet coloration is much more characteristic, and that traces of iron do not interfere. It is also more sensitive, since a distinct reaction is given with the 1/1000 mg. of nickel in 30 c.c. of solution. Cobalt gives with the same reagent a yellow coloration which only interferes seriously with the nickel estimation when the amount of cobalt present is more than twice that of the nickel. The estimation of very small quantities of manganese is often of importance, and Tarugi⁶ has described a new method based on the fact that manganous hydroxide dissolves in glycerol and that

¹ *Ann. Report*, 1905, **2**, 190.

³ *J. Soc. Chem. Ind.*, 1906, **25**, 397.

⁵ *Proc. Roy. Soc.*, 1906, **77**, B, 420.

² *Bull. Soc. chim.*, 1906, [iii], **35**, 293.

⁴ *Ann. Report*, 1905, 186.

⁶ *Gazzetta*, 1906, **36**, i, 332.

the resulting solution readily oxidises with the formation of a ruby red colour, which can be made the basis of a colorimetric process. The reaction appears to be capable of indicating as little as 0.0000005 gram of manganese.

Hydrazine has, during recent years, been recommended in a number of cases for the volumetric estimation of certain of the metals, and Rimini¹ has described, for the estimation of mercury and also of persulphates, volumetric processes involving the use of that reagent which appear to be accurate, and, in the case of persulphates more especially, useful.

The estimation of cadmium as sulphide leaves much to be desired in point of accuracy, and Baubigny² deals very fully with the conditions necessary for the exact conversion of the sulphide into sulphate, a form in which, as many analysts know, this metal may, like zinc, with advantage be weighed. C. Goldschmidt³ records the interesting observation that cadmium is quantitatively precipitated when solutions of its salts are boiled in aluminium vessels in the presence of a trace of chromium nitrate or cobalt nitrate, the aluminium acting catalytically just as nickel and cobalt do in the case of gold and silver respectively. Whilst the volumetric estimation of zinc would scarcely be resorted to when great accuracy is desired, it is sometimes capable of being employed with advantage in technical work. Two papers on this subject may be usefully referred to, one by Deckers,⁴ on the sodium sulphide method, and the other by Murmann,⁵ who has studied the conditions under which the best results can be obtained by titrating with ferrocyanide, using uranyl chloride as indicator.

Czerwek⁶ describes a method for the separation of tin and antimony based upon the formation of a double compound of stannic acid and phosphoric acid. The method appears to be not only convenient but accurate, and will doubtless be submitted to a careful examination.

The various gravimetric methods for the estimation of calcium have been criticised in a paper by Brunck,⁷ who recommends the conversion of the ignited oxalate into fluoride by treatment with hydrofluoric acid solution.

Several papers have been published during the year dealing with the use of zinc as reducing agent for ferric salts prior to titration with bichromate or permanganate. In this connexion the author may, perhaps, be permitted to point out the great advantage of using palladium-hydrogen (charged palladium) for this purpose, and to

¹ *Atti R. Accad. Lincei*, 1906, [v], 15, ii, 320.

² *Compt. rend.*, 1906, 142, 577, 792, and 959.

³ *Zeit. anal. Chem.*, 1906, 45, 344.

⁴ *Bull. Soc. chim. Belg.*, 1906, 20, 164.

⁵ *Zeit. anal. Chem.*, 1906, 45, 174.

⁶ *Ibid.*, 505.

⁷ *Ibid.*, 77.

express his surprise that so few analysts should avail themselves of this clean and useful method.

All who regard chemical analysis as an important branch of the science of Chemistry and not merely as a useful art will read with much interest a paper by Bruni and Padoa¹ on the conditions affecting the precipitation and solution of metallic sulphides. These authors have experimentally demonstrated the correctness of Ostwald's prediction, based on a consideration of the law of mass action and the hypothesis of electrolytic dissociation, that by causing hydrogen sulphide to react under pressure, it would be possible to precipitate from acid solutions the sulphide of those metals, for example, iron, cadmium, cobalt, and nickel, which, in ordinary circumstances, are more or less readily soluble in acid. On the other hand, by diminishing the pressure cadmium sulphide is found not to be precipitated from solutions which yielded precipitates under ordinary conditions.

Following Stähler and Scharfenberg,² Moser³ has studied the phosphate method for the estimation of bismuth and its separation from certain other metals, and his paper may be read with advantage.

Funk⁴ has studied the separation of iron from manganese, nickel, cobalt, and zinc, and in his second communication shows that the formic acid process in which the iron is precipitated as a basic ferric formate is preferable to the acetate method, since the metals remaining in solution after the separation of the iron are amenable to more direct treatment.

Jannasch and Gottschalk⁵ have studied the use of ozone in quantitative analysis, and have shown that it affords an accurate method for the estimation of manganese, and that this metal may be quantitatively separated by its aid from a number of others, including zinc and cadmium. The reducing activity of hydrogen has been made the subject of further study by the author of this report and H. D. Law,⁶ and it has been shown that the efficiency of the hydrogen obtained by the interaction of metals and acids is dependent on a number of factors, both chemical and physical in their nature, but that among these the question of "potential" or "supertension" plays an important part. A special study has been made of the Marsh-Berzelius process as applied to the estimation of traces of arsenic, and it has been shown that whilst certain metals, such as platinum, iron, and copper, lower the "potential" at which the hydrogen is evolved and so diminish the sensitiveness and accuracy of the method, other metals, such as cadmium and tin, do not produce this effect. In this way the so-called 'insensitiveness' of many samples

¹ *Atti R. Accad. Lincei*, 1905, [v], 14, ii, 525.

² *Zeit. anal. Chem.*, 1906, 45, 19.

³ *J. pr. Chem.*, 1906, [ii], 73, 497.

⁴ *Ber.*, 1905, 38, 3862.

⁵ *Ibid.*, 181 and 489.

⁶ *Analyst*, 1906, 31, 3.

of commercially pure zinc which frequently contain traces of iron is explained. Several papers dealing with the estimation of arsenic by the modified Marsh method have been published during the year, and whilst these do not as a rule contain anything that is really new, some of the authors, notably Vámosy,¹ Gautier,² and Bishop,³ either recommend the addition of platinum or copper salts as "accelerators," or the use of copper-coated zinc in the hydrogen generation flask. Of course, when comparatively large quantities (several milligrams) of arsenic are in question, the error introduced is not, perhaps, serious, but when fractions of a milligram have to be estimated it is full time that the inadmissibility of such additions was recognised. Two papers which are worthy of attention and which deal with the titration of solutions of hydrofluosilicic acid have been published, the one by Sahlbom and Hinrichsen,⁴ and the other by Schucht and Möller.⁵ The influence of dissociation on the results obtained by titration with alkali under varying conditions is very interesting and instructive.

Glucinum salts, like those of ferric iron, chromium, and aluminium, liberate iodine from solutions containing iodide and iodate, the hydroxide being at the same time precipitated. Glasmann⁶ bases on this fact a method for the estimation of glucinum which appears to give very accurate results. The method described by the same author⁷ for the separation of glucinum and aluminium is sometimes a useful one, but, as has been pointed out by Friedheim,⁸ it is old and perfectly well known to analysts.

Titanium trichloride, which appears to have been first employed in analytical procedure by Knecht, is, as is well known, a powerful reducing agent, and Rhead⁹ has applied it to the volumetric estimation of copper. The end point is sharper than in the iodide method,¹⁰ and the test results are good.

In the electrochemical branch of analytical chemistry there is comparatively little of importance that is new to record. Owing to the many obvious advantages which electrochemical estimations and separations present to the analyst, a large and increasing amount of attention is now being paid to the improvement of apparatus and to the sharper definition of the working conditions necessary for success, but the greater part of such work, important though it is, scarcely calls for special notice in this report. Foerster¹¹ shows that by working at a potential (2.05 volts) below that at which hydrogen is

¹ *Bull. Soc. chim.*, 1906, [iii], 35, 24.

² *Ibid.*, 207.

³ *J. Amer. Chem. Soc.*, 1906, 28, 178.

⁴ *Ber.*, 1906, 39, 2609.

⁵ *Ibid.*, 3693.

⁶ *Ibid.*, 3368.

⁷ *Ibid.*, 3366.

⁸ *Ibid.*, 3868.

⁹ *Trans.*, 1906, 89, 1491.

¹⁰ Gerlinger, *Zeit. angew. Chem.*, 1906, 19, 520.

¹¹ *Ber.*, 1906, 39, 3029.

evolved, it is possible to obtain very good results in the electrolytic estimation of copper in solutions slightly acidified with sulphuric acid, and to separate that metal from others (cadmium, cobalt, nickel, iron, and zinc) which require higher voltages for their deposition. Price and Judge¹ have investigated the deposition of zinc from zinc sulphate solutions, using a rotating cathode, and find that under certain defined conditions very good results can be obtained. The electrolytic precipitation of gold from solutions of the chloride in presence of potassium cyanide and of sodium sulphide, using a rotating anode, has been the subject of study by Withrow,² who finds that the former is, if anything, the better electrolyte for this purpose, although both are capable of giving very good results. The same author has also devoted some attention to the electrolytic estimation of alkali halide, employing a method very similar to that originally suggested by E. F. Smith,³ in which a silver anode is employed and the halogen weighed as silver halide. In Withrow's experiments, a rapidly rotating spiral cathode was employed and excellent results were obtained, the anode consisting of a silver-plated dish.

In no branch of analytical chemistry is more ingenuity devoted to the devising of new appliances and to the improvement of old than in that which concerns itself with the analysis of gases, and in no branch is it more true that as a general rule the piece of apparatus which gives the best results in the hands of any operator is that to which the operator in question is thoroughly accustomed. It is therefore very difficult in many cases to estimate correctly the value of any new piece of apparatus without being practically acquainted with its working. Gautier and Clausmann⁴ call attention to the difficulty in estimating carbon monoxide in mixtures either by cuprous chloride absorption or by the combustion method, and advocate the employment of iodic anhydride,⁵ a substance which is also recommended by Nowicki,⁶ and by Lévy and Pécou,⁷ for the estimation of small quantities of carbon monoxide in air. Franzen⁸ advocates the use of an alkaline solution of sodium hyposulphite as an oxygen absorbent in gas analysis, and points out that in addition to its cheapness it possesses the advantage over the usual reagents of acting efficiently at low temperatures, and of not absorbing carbon monoxide. Collins⁹ describes an improved form of Scheibler's apparatus for the gasometric estimation of carbon dioxide in carbonates, which eliminates several important sources of error inherent in the original form, and permits of its application to problems in which a fairly high degree of accuracy

¹ *Trans. Faraday Soc.*, 1906, **2**, 85.

² *J. Amer. Chem. Soc.*, 1906, **28**, 1350.

³ *Ibid.*, 1903, **25**, 883.

⁴ *Compt. rend.*, 1906, **142**, 485.

⁵ Compare *Compt. rend.*, 1898, **126**, 931.

⁶ *Oesterr. Zeit. Berg. Hütt.*, 1906, **54**, 6.

⁷ *Compt. rend.*, 1906, **142**, 162.

⁸ *Ber.*, 1906, **39**, 2069.

⁹ *J. Soc. Chem. Ind.*, 1906, **25**, 518.

is demanded. Attention is drawn by Stock and Nielsen¹ to the errors which may arise in the analysis of gaseous mixtures rich in one or more constituents owing to the air, dissolved in the absorbing liquids, which is frequently present in quantities sufficiently great seriously to vitiate the results. Moureu² deals with the estimation of rare gases in gaseous mixtures obtained from natural sources, and describes the apparatus he employs.

Organic Analysis.

A good many papers have been published during the year dealing with new reactions of organic compounds, but these, although often useful, have, as a rule, such a very limited application that they scarcely call for notice in this report. An exception may perhaps be made in favour of the following. Sperling³ describes a modification of the isonitroso-reaction of antipyrine and its more important derivatives which is said to be an improvement on the test as recommended in the German Pharmacopœia. Direct tests for the identification of the more important sugars in carbohydrate mixtures are greatly needed, and it is therefore to be regretted that Schoorl and van Kalmthout,⁴ who have submitted to a critical study the colour reactions described by Pinoff,⁵ have arrived at the conclusion that these are not very characteristic. Fenton⁶ describes an extension of the bromomethylfurfuraldehyde test for carbohydrates, which he published a few years ago, as he has found that this substance reacts readily with malonic ester, yielding a strongly fluorescent product, which serves for the detection of hexoses, or of compounds such as glucosides, which yield those carbohydrates on hydrolysis. The qualitative detection of small quantities of lævulose in the presence of comparatively large quantities of dextrose (by other than optical means) is a particularly difficult problem, and one in which Pinoff's colour reactions appear to be of little use. The results obtained by Mulliken in his study of the osazone test, more especially as regards the time required for the formation of a precipitate with the different sugars, have been confirmed by Sherman and Williams,⁷ who have shown the influence which dilution and the presence of other sugars exert on the test as applied to the detection of dextrose and lævulose. Reference may perhaps be made to a paper by Harang⁸ on the detection and estimation of trehalose in fungi and other plants, since it involves the employment of a specific enzyme (trehalase) and is a new instance of an indirect general method which is often of the greatest service in

¹ *Ber.*, 1906, **39**, 3389.

² *Compt. rend.*, 1906, **142**, 44.

³ *Zeit. Oesterr. Apoth.*, 1906, [v], **44**, 51.

⁴ *Ber.*, 1906, **39**, 280.

⁵ *Ibid.*, 1905, **38**, 3308.

⁶ *Proc. Camb. Phil. Soc.*, 1906, **14**, 24.

⁷ *J. Amer. Chem. Soc.*, 1906, **28**, 629.

⁸ *J. Pharm. Chim.*, 1906 [vi], **23**, 16.

arriving at a knowledge of the constituents of commercial carbohydrate mixtures. The work of Hansen and others on the preparation of pure cultures of the various species of *Saccharomycetes* has, in fact, been of the greatest importance to the analyst as affording him a ready means of obtaining the special enzymes necessary. In the case of trehalase it may be noted that advantage is taken of its secretion by the mould *Aspergillus niger*. Raikow and Ürkewitsch¹ point out that sodium hydroxide gives a yellowish-brown coloration with nitrotoluene, but not with nitrobenzene, and it seems possible that the test may be of service in detecting small quantities of toluene in benzene. A test for "saccharin" has been described by Kastle² which is said to be very delicate, and which appears to be worthy of notice inasmuch as salicylic and benzoic acids do not interfere and need not apparently be removed. A delicate test for indole is described by Konto,³ and some colour reactions for distinguishing between proteins, indole, and scatole are given by Steensma,⁴ who confirms the correctness of those published previously by Rohde. The importance of such tests to the physiological chemist is sufficient justification for referring to them in this report. In this connexion attention may perhaps be directed to a method proposed by Herter and M. Louise Foster⁵ for the quantitative separation of indole and scatole, the former being removed as a naphthaquinone compound. New alkaloidal colour tests are ever forthcoming, but the great majority of these are of little practical use, in that they are either not sufficiently characteristic or are only definite when applied to the pure alkaloid, which is so rarely obtained in laboratory practice. In this branch of analytical chemistry Reichard is indefatigable, and it will perhaps suffice if notice is taken in passing of papers by that author dealing with some new colour reactions of berberine,⁶ a new reaction for morphine,⁷ some new tests for cocaine,⁸ for quinoidine,⁹ and for thebaine.¹⁰ In papers by Bredemann¹¹ on the alkaloids of the rhizome of *Veratrum album*, a number of reactions of the various alkaloids present are described. Lemaire¹² describes some distinctive reactions of alypine (benzoyltetramethyldiaminopentanol hydrochloride) which enable one readily to distinguish between that substance and cocaine, stovaine, and other active therapeutic agents. The identification of artificial organic dyestuffs, more especially when two or more are present, is a problem which is daily becoming more difficult. Various schemes have been proposed for this purpose,

¹ *Chem. Zeit.*, 1906, **30**, 295.³ *Zeit. physiol. Chem.*, 1906, **48**, 185.⁶ *J. Biol. Chem.*, 1906, **2**, 267.⁷ *Ibid.*, 247.⁸ *Ibid.*, 347, and *Pharm. Zeit.*, 1906, **51**, 591.⁹ *Ibid.*, 532.¹⁰ *Pharm. Centr.-H.*, 1906, **47**, 623.¹¹ *Apoth. Zeit.*, 1906, **21**, 41 and 53.¹² *Rep. Pharm.* 1906, **18**, 385.² *Chem. Centr.*, 1906, **i**, 1575.⁴ *Ibid.*, 1906, **47**, 25.⁵ *Pharm. Centr.-H.*, 1906, **47**, 473.

notably by Witt, Weingärtner and Green, and during the past year a further contribution to the subject is made by Gulino¹, who attaches special importance to the behaviour of the dyestuffs with various reducing agents, which is generally recognised as affording one of the best methods of classification.

A number of investigators have, during recent years, attacked the problem of the identification of small quantities of methyl alcohol in the presence of large quantities of ethyl alcohol and with more or less success. The majority of the proposed methods are based on the production of formaldehyde, and its recognition by various colour tests. The difficulty is, however, increased by the fact that these colour reactions are not always characteristic, and in addition a number of organic compounds other than methyl alcohol yield formaldehyde on oxidation, and Scudder and Riggs² point out that this constitutes an objection to the recently published method of Leach and Lythgoe, in which a hot copper spiral is used. Voisenet³ has described an oxidation method in which the formaldehyde is recognised by a test which is said to be quite characteristic if carried out as recommended, but to what extent the second of the above difficulties may apply cannot be determined until the method has been more extensively tried. In this connexion it may be noted that Leys⁴ has described a mercury reagent which is said to admit of a ready distinction between acetaldehyde and formaldehyde in very dilute solutions.

That the method usually adopted for the combustion of organic compounds in elementary organic analysis leaves much to be desired in respect of convenience of working, neatness, and cleanliness is fully recognised, and a number of workers have introduced improvements more especially in the direction of employing "contact" substances and heating by electricity. In my previous report⁵ reference was made to papers by Dennstedt in which he advocated the use of an electric furnace and specially-devised tubes. These suggestions have been criticised by Holde,⁶ who has failed to obtain good results in certain cases with the form of furnace recommended by Dennstedt, but the latter author in a reply⁷ draws attention to some practical details, the observance of which is essential for success. The method proposed by Carrasco,⁸ and slightly modified by that author and Plancher,⁹ is simpler, inasmuch as the combustion is brought about by a heated platinum spiral in an atmosphere of oxygen, and the

¹ *Zeit. Farb. Text. Ind.*, 1906, **5**, 337.

² *J. Amer. Chem. Soc.*, 1906, **28**, 1202.

³ *Bull. Soc. chim.*, 1906, [iii], **35**, 748.

⁴ *Ann. Chim. anal.*, 1906, **11**, 84.

⁵ *Ann. Report*, 1905, 195.

⁶ *Ber.*, 1906, **39**, 1615.

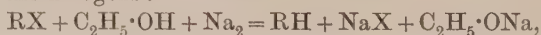
⁷ *Ibid.*, 1623.

⁸ *Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 608.

⁹ *Ibid.*, 613.

apparatus is very compact and neat. The results are good, the working expeditious, and the method is applicable to substances containing nitrogen, halogens, and sulphur. This method is similar in principle to that devised by Morse and Taylor referred to in my last report, and which has now been modified by Morse and Gray¹ to admit of the simultaneous estimation of carbon, hydrogen, and sulphur. These papers may be read with advantage by all chemists who are frequently called on to make organic combustions, and who are working in laboratories where the electric current is available.

Vaubel and Scheuer² recommend for the estimation of halogens in organic compounds a simple method in which the compound is heated with concentrated sulphuric acid in the presence of excess of sulphurous acid. The halogen is obtained either as the element or as the hydric acid, and is converted directly into the silver halide. This method, although not applicable to very volatile substances, appears to be a useful one in many cases, and gives good results. For the same purpose Stepanoff³ proposes a method in which the substance is heated with metallic sodium and ethyl alcohol. The reaction proceeds according to the following general equation, in which "X" stands for one of the halogens:



and the method which is said to be almost universally applicable gives apparently accurate results.

Some years ago Dunstan and Carr found that the nitrogen in aconitine could not be accurately estimated by the ordinary Dumas combustion method, inasmuch as the nitrogen in the measuring vessel was always accompanied by methane. Haas⁴ finds that a number of organic bases behave in a similar manner, but that correct results can be obtained if lead chromate is substituted for the copper oxide, and if the substance is mixed prior to combustion with a sufficient quantity of cuprous chloride. In view of the fact that Dumas' method is always regarded as the standard one, this communication is obviously of considerable importance. In order to avoid the somewhat large percentage error inseparable from the weighing of very small quantities of carbon dioxide in potash bulbs, McFarlane and Gregory⁵ advocate barium hydroxide absorption, as in the well-known Pettenkofer's method, and the conversion of the barium carbonate into sulphate. When rather larger quantities of carbon dioxide are in question, the authors make use of an ammoniacal barium chloride solution for absorption. The principles involved are of course well known, but the method is one that might be more often employed

¹ *Amer. Chem. J.*, 1906, **35**, 451.

² *Chem. Zeit.*, 1906, **30**, 167.

³ *Ber.*, 1906, **39**, 4056.

⁴ *Trans.*, 1906, **89**, 570.

⁵ *Chem. News*, 1906, **94**, 133.

in the estimation of small quantities of carbon, such as have to be dealt with, for example, in steel analysis.

Watson Smith, jun.,¹ has introduced certain modifications into Strache's well-known phenylhydrazine method for the determination of the carbonyl groups in organic compounds which are said considerably to improve the process.

The estimation of the percentage of methyl alcohol in commercial formaldehyde solutions is sometimes of importance, and for this purpose Blank and Finkenbeiner² recommend a process based on oxidation by means of chromic acid and the indirect determination of the amount of oxygen used. Vanino and Seitter's method for the estimation of formaldehyde by oxidation with permanganate in acid solution in the cold has been studied by Grossmann and Aufrecht,³ who find that it gives good results if sufficient time is allowed for the completion of the reaction. Formic acid is also completely oxidised in acid solutions by permanganate, but Rupp⁴ shows that the reaction proceeds more rapidly in alkaline solutions.

For the estimation of acetone in wood spirit, crude acetone, and similar liquids, Auld⁵ has devised a new method depending on the formation of bromoform, its subsequent hydrolysis with alcoholic potash, and the volumetric estimation of the bromine by means of silver solution. This method appears to be capable of giving good results, and it possesses several obvious advantages over the various modifications of the iodoform process.

Jolles⁶ has applied the bisulphite reaction to the estimation of acetone, and given a sufficiently lengthy period of contact the results are good.

No year passes without a number of new processes being put forward for the estimation of the reducing sugars. Occasionally some of these are useful in special cases, and frequently they are characterised by considerable ingenuity; but generally speaking it may be said that no process approaches in point of accuracy the gravimetric Fehling method when properly carried out, and certainly none is so generally applicable. C. A. Browne, jun.,⁷ points out that the cupric-reducing power of a sugar is constant for all concentrations if the excess of copper remaining in solution is kept constant, and that the ratio of the weights of two sugars which reduce the same amount of copper is a constant one at all concentrations. The author has determined the value of this ratio for a number of sugars (compared with dextrose as a standard) and finds, notwithstanding statements to the contrary, that the "dextrose equivalent" of a mixture of reducing sugars is

¹ *Chem. News*, 1906, **93**, 83.

² *Ber.*, 1906, **39**, 1326.

³ *Ibid.*, 2455.

⁴ *Zeit. anal. Chem.*, 1906, **45**, 687.

⁵ *J. Soc. Chem. Ind.*, 1906, **25**, 100.

⁶ *Ber.*, 1906, **39**, 1306.

⁷ *J. Amer. Chem. Soc.*, 1906, **28**, 439.

equal to the sum of the "dextrose equivalents" of the constituents. The disturbing effect of sucrose is dealt with in this paper, and also in a communication by Munson and Walker,¹ who have suggested a set of standard conditions for the carrying out of the reduction process, and have drawn up tables for the use of operators observing the conditions they lay down. Pieraerts² shows that raffinose can be completely hydrolysed to melibiose and lævulose by citric acid under suitable conditions, and has based on this fact a method for the polarimetric estimation of sucrose and raffinose when present together. Mlle. Talon³ calls attention to a possible source of error in the estimation of sugar in liquids containing much alcohol, since during the acid hydrolysis process esters of dextrose are produced which appreciably influence the results obtained by the reduction process or by the polarimeter.

The detection and estimation of adulterants in oil of turpentine constitutes an analytical problem of some importance and frequently of great difficulty. The "bromine absorption" has often been advocated as a trustworthy test, but, as Utz⁴ has pointed out, the variations in the genuine oil are great, and some resin oils so nearly approach turpentine in this respect that considerable proportions might be present, and yet not reduce the bromine value below that of certain pure oils. A paper has been published by Böhme⁵ on the same subject, in which an improved method is recommended for the estimation of paraffin and benzene hydrocarbons in turpentine by the well-known sulphuric acid process. Valenta⁶ finds that methyl sulphate readily dissolves aromatic hydrocarbons such as occur in tar oils, but not paraffin hydrocarbons or resin oils, and has based on this observation a method for the estimation of the former when admixed with the latter which promises to be of considerable service. It will be interesting to see whether the use of this reagent cannot be extended to the analytical examination of other hydrocarbon mixtures. In connexion with hydrocarbon oils, attention may be directed to a paper by Ross and Leather⁷ in which the problem of the valuation of oils used for gas-making purposes is very fully dealt with. The results of the examination of a considerable number of oils by a laboratory method which the authors recommend are given and are compared with those yielded in practical working.

Much useful work has been devoted during the year to the study of essential oils, not the least important being the determination of the analytical 'constants' of genuine samples of those oils, which on account

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 663.

² *Bull. Assoc. Chim. Sucr. Dist.*, 1906, **23**, 1261.

³ *Ann. Chim. anal.*, 1906, **11**, 244.

⁴ *Chem. Rev. Fett. Harz. Ind.*, 1906, **13**, 161.

⁵ *Ibid.*, 266.

⁶ *Chem. Zeit.*, 1906, **30**, 633.

⁷ *Analyst* 1906, **31**, 284.

of their high price are most liable to sophistication. Valuable as this is to the analyst who is specially concerned with this branch of analysis, it is scarcely of sufficient general interest to justify reference to it in this report.

The accurate estimation of tannin in raw materials is another important problem to the solution of which a considerable amount of energy has been devoted. Wislicenus¹ has now arranged for the manufacture on the large scale of "porous alumina" of uniform quality, and describes a form of apparatus by which the process of analysis can be best carried out. The absorptive power of this alumina for colouring matters appears to constitute one objection to its employment, and there seems to be an impression among those best able to judge that it possesses no real advantage over the chromed hide-powder method, which in the form adopted by the American Leather Chemists' Association will probably be recognised as the standard process. Those who are specially concerned with this question will read with interest papers by Small,² Parker and Bennett,³ Procter and Bennett,⁴ and Kopecky.⁵

Several papers dealing with the analysis of explosives have appeared during the year, but of these attention need only be drawn to one by Silberrad, Phillips, and Merriman⁶ on the direct estimation of 'nitroglycerine' in cordite and allied explosives, and which is based on the reduction of the saponification products of the 'nitroglycerine' and the titration of the resulting ammonia.

The estimation of indigotin in commercial indigo is obviously a matter of very great importance to the dyeing trade and judging from several papers recently published the problem does not yet appear to have been finally solved. Numerous methods have been from time to time proposed, but only those depending on the oxidation or reduction of sulphonated indigos appear to be capable of yielding good results, and are in anything like general use. In a critical paper by Bergtheil and Briggs⁷ it is claimed that the permanganate method as worked out by Rawson with slight modifications is capable of yielding concordant and trustworthy figures. The use of barium chloride as a precipitant is, however, shown to be inadmissible, and the authors recommend the employment of freshly precipitated barium sulphate for the purpose of removing impurities. On the other hand, W. P. Bloxam⁸ maintains that correct results cannot be so obtained, and recommends a process based on the separation of the indigotin as potassium indigotintetrasulphonate. It is clear that, in spite of the large amount of valuable work done by the above chemists, a generally

¹ *Collegium*, 1906, 77.

³ *Ibid.*, 1193.

⁴ *Ibid.*, 1203.

⁶ *J. Soc. Chem. Ind.*, 1906, 25, 628.

² *J. Soc. Chem. Ind.*, 1906, 25, 296.

⁵ *Collegium*, 1906, 97 *et seq.*

⁷ *Ibid.*, 729.

⁸ *Ibid.*, 735.

acceptable process has not yet been worked out, and the results of further study of this subject will be awaited with interest.

Analysis of Foods and Drugs.

Dealing first with that most important food product, milk, several papers of importance to analysts have appeared during the year. The method devised by T. E. Thorpe for the analysis of samples of milk (sour and otherwise decomposed) referred to the Government Laboratory under the provisions of the Sale of Food and Drugs Acts, and which was noticed in my previous report¹ has been submitted to a critical study by Richmond and Miller,² who have shown that whilst in certain cases a somewhat closer approximation to the fresh milk values could be arrived at by an extension of the Government Laboratory process, that method is capable of yielding results which are substantially accurate. In those comparatively rare instances where unusually high proportions of butyric or propionic acids are formed, the method appears to be susceptible of improvement. It is generally admitted, however, that the process is one of great practical value, and it has to be borne in mind that it could not be complicated beyond a certain point without seriously reducing its usefulness. In this connexion it is interesting to note that according to Tice and Sherman³ the character of the decomposition changes occurring in milk on keeping is largely determined by the nature of the added antiseptic when such substances have been used. In the presence of 0.07 per cent. to 0.1 per cent. of formaldehyde, although bacterial action appeared to be entirely suppressed, extensive proteolysis occurred with very little loss of milk-sugar, whilst in the presence of sodium fluoride or salicylate a large proportion of the sugar underwent decomposition before any marked digestion of the casein took place. Two other papers by Richmond⁴ are of interest in view of the preparation of so-called homogenised milk, and the very extensive use which is now being made of dried milk or milk powder. In the first place, he gives a series of analyses which seem to show that the Adam's coil method when applied to the analysis of homogenised milk gives results appreciably below those yielded by the Gottlieb, Werner-Schmid, or Gerber methods, and in the second he calls attention, *inter alia*, to the impossibility of extracting the fat directly from milk powders and recommends the Werner-Schmid method. The danger of applying direct extraction methods to the analysis of certain milk-containing mixtures, such as infants' foods, is one which ought not to be overlooked.

¹ *Ann. Report*, 1905, 203.

³ *J. Amer. Chem. Soc.*, 1906, **28**, 189.

² *Analyst*, 1906, **31**, 317.

⁴ *Analyst*, 1906, **31**, 218, 219.

In his annual communication on the composition of milk Richmond¹ states that the average percentage of fat in nearly 15,000 samples analysed during 1905 was 3.73 per cent. with 8.97 per cent. of non-fatty solids. These numbers are almost identical with those of the previous year. For the determination of proteins in milk and of casein in cheese, Trillat and Sauton² recommend a method based on the fact that formaldehyde renders the proteins insoluble without altering their weight, and so permits of their gravimetric estimation. Schrott-Fiechtl³ has compared Gottlieb's, Gerber's, and the Wollny refractometer methods for the estimation of fat in milk, and, as the result of a large number of analyses, has come to the conclusion that all three yield quite trustworthy results. Siegfeld⁴ points out, however, that in the case of machine-separated milks, the cholesterol and lecithin which are extracted by the solvents used in the Gottlieb method introduce an appreciable error into the fat determination. If a simple chemical method for the recognition of milk derived from diseased cows could be devised it would obviously be of the highest importance from the public health point of view. The difficulties appertaining to the solution of this problem will be apparent to all who have any knowledge of the bacteriology of milk, and it will be interesting to see to what extent a determination of the "catalase number" as proposed by Lam in a paper communicated to the sixth International Congress of Applied Chemistry⁵ supplies this want. The detection and estimation of cocoanut oil in butter is a problem which is even more difficult than was at first supposed, and which cannot yet be said to have been satisfactorily solved. In my last report⁶ I called attention to the work of K. Jensen, Kirschner, and O. Jensen on this subject, pointing out that these authors had endeavoured to base, on the differences in the proportions of octoic and butyric acids occurring in butter-fat and cocoanut oil respectively, and in the comparatively sparing solubility of silver octoate, a method for the detection and estimation of cocoanut oil. The hopes which were raised by the publication of these papers have not altogether been realised, and many analysts who have had much experience in this branch of analysis have been led to regard the so-called silver numbers as of very little value. Wijsman and Reijst⁷ have suggested a modification, or rather an extension, of the Jensen method in which the Reichert-Meissl distillate is divided into two unequal portions with the object of obtaining more widely separated solubility differences for the silver salts. The numbers given by the authors did not, however, appear

¹ *Analyst*, 1906, **31**, 176.

² *Compt. rend.*, 1906, **142**, 794, and **143**, 61.

³ *Milchw. Zentr.*, 1906, **2**, 13.

⁴ *Ibid.*, 1.

⁵ *Chemist and Druggist*, 1906, **68**, 914.

⁶ *Ann. Report*, 1905, 204.

⁷ *Zeit. Nahr. Genussm.*, 1906, **11**, 267.

very convincing, and the process has since been adversely criticised both by Jean¹ and by Lührig.² Lewkowitsch, in a private communication to the author of this report, also states that he has obtained conflicting and untrustworthy results. After all it would appear that the Polenske method and the phytosterol acetate test³ still furnish the analyst with the most trustworthy indications, and if in addition the iodine value and refraction numbers are determined, a very near approach to certainty is obtained. It may perhaps be pointed out in opposition to a rather widespread belief that the degree of fluidity of the insoluble volatile acids obtained in any of the distillation processes is of very little diagnostic value.

Bellier⁴ proposes for the detection of cocoanut oil in butter a method based on the precipitation of the fatty acids by means of copper sulphate solution, and claims that by its employment 5 per cent. of cocoanut oil can be detected with certainty. The analytical differences given by the author, and on which the detection of adulteration depends, are very small, but the process will doubtless be carefully examined.

A. W. Thorp⁵ has proposed to substitute for the methods of Polenske and of Muntz and Coudon a simplified procedure which is really only an extension of the ordinary Reichert-Wollny process. This is based on the same principle as that underlying the methods above referred to, but does not involve the use of special apparatus, and, judging from the test analyses recorded, is capable of giving very useful results. Jean⁶ calls attention to the somewhat extensive employment of Karité or Fulwar butter (the fat obtained from the seeds of *Bassia butyracea*) for the purpose of adulterating butter, a fact which still further complicates the analysis of that food product. He gives the analytical "constants" of this fat, and indicates the manner in which the various butter values are affected by its use as an adulterant.

In connexion with the detection and estimation of preservatives in food-stuffs there is not much that calls for special notice. It is well known that sulphur dioxide enters into combination with some of the constituents of certain foods, and that only a proportion of the amount actually present can in some instances be estimated by the ordinary distillation process. It is interesting to note that in certain meats, for example, Holley⁷ was able to recover only about one-fourth of the amount added as sodium sulphite. For the detection of fluorine in foods, Ville and Derrien⁸ propose a new

¹ *Ann. Chim. anal.*, 1906, **11**, 121.

² *Zeit. Nahr. Genussm.*, 1906, **12**, 588.

³ Compare Lührig, *Zeit. Nahr. Genussm.*, 1906, **11**, 11.

⁴ *Ann. Chim. anal.*, 1906, **11**, 412.

⁵ *Analyst*, 1906, **31**, 173.

⁶ *Ann. Chim. anal.*, 1906, **11**, 201.

⁷ *J. Amer. Chem. Soc.*, 1906, **28**, 993.

⁸ *Bull. Soc. chim.*, 1906, [iii], **35**, 239.

method based on the change in the absorption spectrum of methæmoglobin brought about by the addition of fluorine compounds. The test is interesting on account of its novelty, but it remains to be seen whether it is capable of replacing to any extent the methods now in use. It is also of interest to note in passing that the well known colour reaction which formaldehyde gives with proteins in the presence of sulphuric acid containing traces of certain oxidising agents, and which is so largely used in the testing of milk, depends on the presence of the tryptophan (indole) group, and that when that group is absent, as, for instance, in gelatin, no reaction is obtained.¹ In view of the fact that in some countries the use of formaldehyde as a food preservative is either partially or entirely prohibited, the observation of Perrier² that cider and various smoked foods may naturally contain more than 2 milligrams of formaldehyde per 100 grams is of importance. It is to be remarked that this observer has relied upon Voisenet's colour reaction, and it is not impossible that the colorations he obtained may have been due to some other substance than formaldehyde. In any case the observation is an interesting one to public and other analysts who are concerned in the examination of food stuffs under the provisions of adulteration Acts.

The question of the detection of beef-fat in lard has occupied the attention of Dunlop,³ who has shown that the indications of the Belfield crystal test must be accepted with considerable caution, and that the presence of "plumose" groups of crystals, as observed with a low magnifying power, is not to be taken as evidence of beef stearin, unless the characteristic form of individual crystals can be recognised with a higher magnification. In view of the fact that lard obtained from pigs fed on cotton seed meal gives the Halphen reaction, this test is of little value as a proof of adulteration. Farnsteiner, Lendrich, and Büttenberg⁴ have made recent experiments on this point and have found that, although the lard from pigs fed on cotton seed meal often gave a strong Halphen reaction, the melting point of the acetate obtained by Bömer's method showed that cotton seed oil itself could not have been present. The glycogen in horse flesh apparently remains unchanged for a long time, whilst that contained in beef, veal, and pork almost entirely disappears within a few days of the death of the animal. On this fact Martin⁵ bases a method for the detection of horse flesh in sausages and potted meats, the glycogen being estimated by Pflüger's method. In this connexion attention may perhaps be directed to a paper by Pflüger on the estimation of glycogen,⁶ and to a series of communications on the same subject by Desmoulière.⁷

¹ Rosenheim, *Biochem. J.*, 1906, **1**, 233.

² *Compt. rend.*, 1906, **143**, 600.

³ *J. Soc. Chem. Ind.*, 1906, **25**, 458.

⁴ *Zeit. Nahr. Genussm.*, 1906, **11**, 1.

⁵ *Ibid.*, 249.

⁶ *Pflüger's Archiv*, 1906, **114**, 231.

⁷ *J. Pharm. Chim.*, 1906, [vi], **23**, 244, 281, and 332.

The detection and estimation of free mineral acid in vinegar is at the present time of academic rather than of practical interest. Attention may, however, be directed to a paper by Richardson and Bowen,¹ inasmuch as these authors deal in some detail with the influence which the alkaline and earthy phosphates in the ash exert on the results obtained by Hehner's well-known method, and indicate the nature of the approximate correction to be applied.

Much work has been devoted from time to time to the question of the estimation of the higher alcohols in spirits, and much still remains to be done. Veley² has recently made a special study of the Röse-Herzfeld and sulphuric acid colorimetric processes, and finds that both, but more especially the latter, are untrustworthy. Schidrowitz and Kaye,³ in continuation of their critical examination of some of the better known methods, have further studied the Allen-Marquardt process, and are of opinion that carried out under proper conditions it is capable of giving quite trustworthy results. It is shown that the usual "mineral acid" titration with methyl-orange as indicator may be dispensed with when it amounts to less than one-tenth of the whole, as it is not due, as is usually supposed, to hydrochloric acid, but apparently to organic acids, some of which are known to have an appreciable effect on the methyl-orange. The same conclusion has been arrived at by Mann and Stacy,⁴ who have also studied the influence of temperature on the proportion of ethyl alcohol extracted by the carbon tetrachloride. It is in the very nature of things impossible that an exact method should be devised for the estimation of a group of substances such as the so-called higher alcohols, but there can be no doubt that, of all the methods which have been proposed, that of Marquardt, as modified by Allen, is for several reasons the best. It is at least based on scientific principles, and has the further great merit of yielding actual oxidation products which can be examined and, if desired, identified.

Numerous papers dealing with the analytical examination of drugs have, as usual, appeared during the year, but the majority of these, whilst undoubtedly useful, are scarcely of sufficient importance or general interest to warrant a special reference.

Staněk⁵ finds that betaine and choline, which frequently occur together in plants, can be separated almost quantitatively as periodides, the betaine periodide only crystallising from acid solutions whilst the corresponding choline compound also crystallises from liquids which are neutral or slightly alkaline. The test analyses are fairly good, and the method appears to be a useful one.

¹ *J. Soc. Chem. Ind.*, 1906, **25**, 836.

² *Ibid.*, 398.

³ *Analyst*, 1906, **31**, 181.

⁴ *J. Soc. Chem. Ind.*, 1906, **25**, 1125.

⁵ *Zeit. physiol. Chem.*, 1906, **47**, 83.

The testing of glycerol for traces of arsenic is a problem of somewhat frequent occurrence, and Galimard and Verdier¹ call attention to the fact that arsenic is sometimes present in a form (? glyceryl-arsenite), in which it cannot be detected by the direct application of the Marsh method, preliminary treatment being necessary.

Keller's nitric acid oxidation method for the separation of brucine and strychnine has been studied by Reynolds and Sutcliffe,² who find that accurate results can be obtained by the process as modified by Stoeder or by Gordin if certain details of procedure to which they direct attention are observed.

The testing of disinfectants, of which there are now so many on the market, is clearly a matter of considerable importance, and the adoption of bacteriological methods such as that of Rideal and Walker³ marks a great advance on the unsatisfactory chemical methods formerly in use. In the above-mentioned process the germicidal value of the disinfectant in relation to that of phenol ("carbolic acid coefficient") is determined in water, but Lloyd⁴ and M. W. Blyth⁵ have shown that in the presence of organic matter, such as milk or urine, quite different results are obtained, and that two disinfectants may occupy very different positions in a table of relative "efficiencies," according as the test is made with water, or with, say, diluted milk.

Toxicological Analysis.

Only a few communications need be referred to in this branch of analytical chemistry.

Ipsen-Innsbruck⁶ has studied atropine from the toxicological point of view, and finds that it is rapidly absorbed by all parts of the body and distributed in the blood. He also finds that the alkaloid is possessed of very great stability in the presence of decomposing organic matters, and that 0.03 gram of atropine, after remaining in contact with decomposing blood for twelve years, could still be detected. Sarda and Caffart⁷ describe a method of treating blood stains for purposes of identification, in which chlorohæmatin is obtained, the crystals of which can be easily recognised by the aid of the microscope. The method is said to work well with very old stains, and to be preferable to those in ordinary use. In this connexion, attention may be directed to a paper by Carlson⁸ on the guaiacum test for blood, and to one on the catalase test for blood stains by van Itallie.⁹ The serum test for

¹ *J. Pharm. Chim.*, 1906 [vi], **23**, 183.

² *J. Soc. Chem. Ind.*, 1906, **25**, 512.

³ *J. Sanit. Inst.*, 1903, 424.

⁴ *J. Soc. Chem. Ind.*, 1906, **25**, 405.

⁵ *Analyst*, 1906, **31**, 150.

⁶ *Zeit. angew. Chem.*, 1906, **19**, 141.

⁷ *Compt. rend.*, 1906, **143**, 251.

⁸ *Zeit. physiol. Chem.*, 1906, **48**, 69.

⁹ *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**, 628.

differentiating the blood of different animals has also been studied by Piorkowski,¹ who has devised a simplified method of applying it. Bettink and van den Driessen Mareeuw² have dealt with the identification of chloral hydrate obtained from parts of dead bodies, and have proposed a method for its estimation in such material which is said to give better results than that of Kippenberger. T. E. Thorpe³ has devoted attention to the estimation of arsenic in wall-papers, fabrics, and similar materials, and finds that the electrolytic method as employed in the Government Laboratory, preceded by appropriate treatment of the substance, is capable of giving good results.

This report would hardly be complete without some reference to the sixth International Congress of Applied Chemistry held in Rome at the end of April. More than fifty papers were presented to the section concerned with analytical chemistry, and many more were communicated to other sections, notably that dealing with bromatology. To one of these reference has already been made, but many have not yet been officially published, and cannot therefore be discussed. A number of the sections have adopted resolutions, many of which embody most useful suggestions, although others cannot be regarded as anything but aspirations towards ideals which are scarcely likely to be realised. Of particular importance to analysts is the very marked leaning of some of the sections towards uniformity and standardisation of analytical procedure. It cannot be denied that there is much to be said in favour of the standardisation of many arbitrary methods employed in the analysis of commercial products, more especially when, as is frequently the case, the results have to serve as the basis of a contract between buyer and seller, or perhaps as the foundation of a criminal prosecution. On the other hand, there has been a marked tendency, which many competent analysts deplore, to prescribe rigidly standardised conditions for the carrying out of many analytical methods which are thoroughly well known, and which in skilled hands are capable of yielding highly accurate results. In the case of all the well known and commonly used processes, the conditions essential for accuracy have been determined and laid down by numerous workers, and no capable analyst will depart very far from them, although he will remember that the exact set of conditions obtaining in one analysis are not often reproduced in another, and he will consequently recognise that a certain amount of latitude is necessary if the best results are to be obtained. Up to a certain point the movement in favour of "unification" and 'standardisation' is good and worthy of support, but beyond that point it must receive the con-

¹ *Ber. Deut. Pharm. Ges.*, 1906, **16**, 226.

² *Pharm. Weekblad*, 1906, **43**, 487.

³ *Trans.*, 1906, **89**, 408.

demnation of all who regard chemical analysis as a highly important branch of applied chemistry and not merely as a useful art.

Apparatus.

In the body of this report reference has been made to certain new appliances, and it does not appear to be necessary to refer to these again. The following list contains references only to those new pieces of apparatus which have been described in recognised journals, and which appear to be of general utility. It may be remarked that the titles are not always exactly those given by the authors, but have been in some cases slightly altered so as to indicate more clearly the nature of the apparatus in question.

"A new gas calorimeter." C. V. Boys (*Proc. Roy. Soc.*, 1906, 77, A, 122).

"Apparatus for removing gases from aerated liquids before determining the specific gravity of the latter." K. Ulrich (*Chem. Zeit.*, 1906, 30, 90).

"On vessels for collecting and transporting samples of gas." R. Nowicki (*Oesterr. Zeit. Berg. Hutt.*, 1906, 54, 62).

"Apparatus for the continuous registration of the results of gas analysis (increase of weight due to absorption)." B. Stollberg (*Chem. Zeit.*, 1906, 30, 347).

"New form of absorption tube for very soluble gases." E. P. Perman (*Chem. News*, 1906, 93, 213).

"Gas analysis apparatus." John S. Haldane (*J. Hygiene*, 1906, 6, 74).

"Modification of the Orsat gas analysis apparatus." Louis de Saint-Martin (*Ann. Chim. anal.*, 1906, 11, 96).

"Simplified measurement and reduction of gases." H. Rebenstorff (*Chem. Zeit.*, 1906, 30, 486).

"New apparatus for the examination of gases, poor in certain constituents, by absorption methods." C. J. Gülich (*Chem. Zeit.*, 1906, 30, 1302).

"A new form of gas generating apparatus." A. W. Gregory (*Chem. News*, 1906, 93, 27).

"A 'continuous-flow' wash bottle" (*Analyst*, 1906, 31, 34).

"A combined wash-bottle and pipette." J. W. Hogarth (*Chem. News*, 1906, 93, 71).

"Weighing-bottle for liquids." K. Buschmann (*Chem. Zeit.*, 1906, 30, 1060).

"Modification of Maquenne's wash-bottle." Antoine Villiers (*Ann. Chim. anal.*, 1906, 11, 211).

"A burette filling device." Edward French (*Chem. News*, 1906, 93, 71).

"A burette top for preventing the absorption of carbon dioxide and other gases" (*Chem. Zeit.*, 1906, 30, 459).

"Struthers syphon pipette" (*Analyst*, 1906, 31, 247).

"New automatic pipette." Stein (*Chem. Zeit.*, 1906, 30, 967).

"Douglass assay tube" (*Analyst*, 1906, 31, 246).

"Filter tubes for collection of precipitates." Samuel L. Penfield and W. M. Bradley (*Amer. J. Sci.*, 1906, [iv], 21, 453).

"A delivery funnel for introducing liquids into vessels under increased or diminished pressure." T. J. Bryan (*J. Amer. Chem. Soc.*, 1906, 28, 80).

"A new vacuum filter for laboratory use, and a novel method for cleaning the filtering material" (*Zeit. angew. Chem.*, 1906, 19, 95).

"Vacuum-filter drying apparatus." Barth (*Chem. Zeit.*, 1906, 30, 907).

"The properties of apparatus (rings, tubes, crucibles, &c.) made of magnesia." Kurt Arndt (*Chem. Zeit.*, 1906, 30, 211; compare E. Wedekind, *Chem. Zeit.*, 1906, 30, 329).

"Porcelain-lined bomb for general laboratory use." S. F. Acree (*Amer. Chem. J.*, 1906, 35, 309).

"A new burner for spectroscopic work." E. H. Riesenfeld and E. H. Wohlers (*Chem. Zeit.*, 1906, 30, 704).

"A new sodium burner" (*Chem. Zeit.*, 1906, 30, 835).

"Alcohol calorimeter for coal testing." W. H. Wallace (*Engineering*, 1906, 81, 527).

"An improved form of the William Thomson calorimeter." Thomas Gray (*J. Soc. Chem. Ind.*, 1906, 25, 409).

"A new laboratory sink." Heinrich Gökkel (*Chem. Zeit.*, 1906, 30, 755).

"Viscosimeter for varnishes." E. Valenta (*Chem. Zeit.*, 1906, 30, 583).

"A new form of calcium chloride tube." A. E. Hill (*Proc.*, 1906, 22, 87).

"A new form of potash bulbs for estimation of carbon dioxide in organic combustions." S. F. Acree (*Amer. Chem. J.*, 1906, 35, 309).

"Two new forms of apparatus for use in organic analysis (azotometer and potash apparatus)." Erwin Rupp (*Zeit. anal. Chem.*, 1906, 45, 558).

"Modification of Liebig's potash bulbs." R. Villiers (*Ann. Chim. anal.*, 1906, 11, 250).

"Improved apparatus for the continuous extraction of liquids with ether." R. S. Bowman (*Proc.*, 1906, 22, 24).

"Apparatus for the complete extraction of liquids containing saccharin." Maurice Duyk (*Ann. Chim. anal.*, 1906, 11, 82).

"A modification of Foerster's fat extraction apparatus." Ernest Pescheck (*Zeit. angew. Chem.*, 1906, 19, 1513).

"New form of platinum parting apparatus." A. Jarman (*Trans. Inst. Mining and Metall.*, 1906, 15, 625).

"Thermometer for low temperatures." A. Stock and C. Nielsen (*Ber.*, 1906, 39, 2066).

"New method for the calibration of thermometers below 0° C." T. W. Richards and F. G. Jackson (*Zeit. physikal. Chem.*, 1906, 56, 362).

"A temperature regulator for use with the immersion refractometer." F. Löwe (*Chem. Zeit.*, 1906, 30, 685).

"A simple form of rotating electrode for use in electrochemical analysis." F. M. Perkin (*Trans. Faraday Soc.*, 1906, 2, 91).

"A new electrolytic apparatus (rotating propeller-like anode)." S. F. Acree (*Amer. Chem. J.*, 1906, 35, 313).

"A new rheostat for electrolytic analysis." G. Pascalis (*Mon. Sci.*, 1906, [iv], 20, 168).

"A modified Westphal balance for solids (particularly cements and minerals) and liquids." F. M. Williams (*J. Amer. Chem. Soc.*, 1906, 28, 185).

"New zero adjustment for chemical balances." J. McDowall (*Chem. News*, 1906, 94, 104).

"Improved Beckmann apparatus for molecular weight determinations." J. M. Sanders (*Proc.*, 1906, 22, 165).

"Portable universal stand for elementary analysis" (*Chem. Zeit.*, 1906, 30, 1045).

"The production of a high vacuum in the Scheibler desiccator." H. C. Gore (*J. Amer. Chem. Soc.*, 1906, 28, 834).

"Apparatus for distilling solids in a vacuum." Hugo Haehn (*Zeit. angew. Chem.*, 1906, 19, 1669).

"Shortened manometer with receivable vacuum (for distillation in a vacuum, &c.)." Leo Ubbelohde (*Chem. Zeit.*, 1906, 30, 966).

"Apparatus for the estimation of sulphur and carbon with single or double receiver." Arthur Wilhelmi (*Zeit. Chem. Apparatenkunde*, 1906, 1, 155).

"Improved apparatus for estimating total sulphur in coal gas; modification of Dreschmidt's method." Everhard P. Harding (*J. Amer. Chem. Soc.*, 1906, 28, 537).

"New apparatus for the estimation of sulphur and carbon (in iron)." A. Kleine (*Zeit. angew. Chem.*, 1906, 19, 1711).

"Percolator for use in assaying drugs." Frank R. Eldred (*J. Amer. Chem. Soc.*, 1906, 28, 187).

"Improved Mayer's apparatus for the evolution of chlorine." (*Zeit. Nahr. Genussm.*, 1906, 12, 221).

"A new urometer; modification of the hypobromite method." William M. Dehn (*Zeit. anal. Chem.*, 1906, 45, 604).

In conclusion, the author would once again remind his readers that the task of selecting from the enormous mass of published matter those communications which appear to contain observations of special importance to analysts is one of increasing difficulty, and, within the limits of a review such as this, many papers embodying the results of really useful work must of necessity remain unnoticed.

ALFRED C. CHAPMAN.

Addendum.

Since the above was written, I have been informed that in July, 1901, H. A. Danne published, in *The Chemist and Druggist of Australasia*, a method for the estimation of moisture identical in principle with Dupré's acetylene method, referred to on page 202 of this report.

A. C. C.

PHYSIOLOGICAL CHEMISTRY.

STEADY progress is the key-note of the work in Physiological Chemistry which has been published since the date of last year's report. It seldom happens that an annual writer is able to point to any great discovery made in the preceding twelve months, and it is not my good fortune to be able to chronicle any such important event this year. Most discoveries are made so slowly, and piece by piece, that it is difficult to assign any date at all to them, and the surest knowledge is always proportional to the pains taken to render each piece accurate. Ehrlich's views, for instance, on immunity problems furnished investigators with a brilliant and fruitful stimulus to further work, and the steady flow of researches on these lines which still continues shows that the stimulus is still effective. But the general theoretical results are at present difficult to see, and it is impossible to bring anything in the way of order out of the apparent chaos. Physical chemistry, again, has its physiological applications; it has enabled us to understand something more than we previously did about the osmotic processes in the body; it has taught us that the action of salts must be viewed in the light of the action of ions; and it has reduced the investigation of even such obscure questions as ferment action to almost mathematical precision.¹ But here again the time is not ripe for generalisation; the physical chemists have many differences of opinion on quite fundamental questions to settle first, and until these are cleared away, the physiologists must be content to wait for the full benefits they expect from this new branch of science.

It will therefore not be to questions of this nature that I shall devote the bulk of what I have to say, although they have, so far as space is concerned, occupied so much of the Chemical Society's Journal and its abstracts. I imagine further that it is not the object of such a report as this to epitomise still further the epitomes which have monthly made up the bulk of the Journal, but

¹ See, for instance, E. F. Armstrong's "Studies in Enzyme Action," Nos. VII and VIII of which have recently appeared (*Proc. Roy. Soc.*, 1905, B, **76**, 592, 600; *Abstr.*, 1906, i, 127, 128).

rather to give the writer, who happens in this case to be also an abstractor, an opportunity to enlarge upon certain aspects of the science with which he happens to be more familiar, and to exercise that right of comment which is denied to him when he merely presents an abstract.

I shall naturally take the abstracts as the foundation of such remarks, and shall endeavour to select those subjects which appear to be most profitable for discussion.

Proteid Chemistry and Proteid Metabolism.

This question still stands, and probably for many years to come will continue to stand, pre-eminent in its importance to the workers who apply themselves to the chemical side of biology.

Nomenclature.—At the outset we meet with a difficulty in the very names applied to the heterogeneous groups of substances included under the word Proteid. The difficulty has become an acute one for teachers and students, so various are the terms that are used by different writers. A committee has consequently been appointed to consider "Proteid Nomenclature," and physiologists and chemists have sat in conclave to formulate something they hope will be acceptable to all. Although their work is not yet concluded, it may not appear premature to state their main decisions.

Our knowledge of the chemistry of the albuminous substances is slowly progressing under Emil Fischer's leadership, and this will no doubt in time enable one to present a classification on a strictly chemical basis. But until that time arrives, we must be content very largely with the artificial classification (on the basis of solubility and so forth) which has hitherto prevailed. The classification suggested must therefore be regarded as a provisional one, which, whilst it retains the old familiar names so far as possible, yet attempts also to incorporate some of the new ideas.

The general name recommended for the whole group is that of Protein. It is at present so used in America, and to some extent in Germany, and has been definitely accepted by Fischer in the volume of his collected papers on the subject which has recently appeared. The word has the advantage of admitting of the derived words, protease, proteose, &c., and it has, after all, the ring of familiarity.

The sub-classes, beginning with the simplest, would be as follows:—

1. Protamines.—These yield a comparatively small number of amino-acids as their cleavage products, and are instanced by such substances as salmine and sturine derived from the sperm of fishes.

Their most abundant cleavage products are diamino-acids; some protamines yield, for instance, over 80 per cent. of their nitrogen in the form of arginine.

2. Histones.—These yield a larger number of amino-acids, but not so many as those in the next classes. They have been separated from blood corpuscles, and are peculiar in being precipitable from solution by ammonia. Classes 1 and 2 probably shade insensibly into one another.

3. Albumins.

4. Globulins.

The albumins and the globulins differ from one another in their solubilities, the globulins being more readily "salted out" than the albumins. They comprise the greater number of native proteins, and all possess the character of being coagulated when their solutions are heated.

5. Sclero-proteins.—This perhaps is the most heterogeneous group of the series; it includes the gelatin and keratin members. The prefix of the new word indicates the skeletal origin and often insoluble nature of these substances. They have in the past been called albuminoids by physiologists, but this word is ambiguous, and is used, and probably will continue to be used, by many chemists as equivalent to protein.

6. Phospho-proteins.—This is the vitellin-caseinogen group. The prefix *nucleo-* frequently used in relation to these substances is both incorrect and misleading.

7. Conjugated proteins.—Here the protein molecule is united to a "prosthetic" group. The principal varieties of these are the nucleo-proteins, the gluco-proteins (*e.g.* mucin), and the chromo-proteins (*e.g.* hæmoglobin).

Coming next to the products of protein-hydrolysis (a term preferable to proteolysis), the Committee recommend that these be classified as follows:—

1. Meta-proteins.

2. Proteoses.

3. Peptones.

4. Polypeptides.

Meta-protein replaces albuminate (acid-albumin, alkali-albumin). The termination *ate* implies a salt, and so is objectionable. These first products are, moreover, obtainable from both albumins and globulins, and the prefix *meta-* is an indication of comparatively slight chemical alteration. The proteoses form the next stage as cleavage continues, and then come the peptones, a household word very unlikely ever to disappear from chemical literature. The term should, however, be restricted to those further products of hydrolysis

which cannot be salted out from solution, but which, nevertheless, still give the biuret reaction.

The polypeptides are still further on the down-grade; although most of those we are acquainted with are synthetical products which Fischer has prepared by linking amino-acids together, some have been discovered as a result of digestive cleavage, and no doubt are the immediate precursors of the final cleavage products, the amino-acids.

It should, however, be noted in conclusion that this classification is mainly applicable to proteins of animal origin. The vegetable proteins may be arranged under the same main headings, although it is doubtful if a real and complete analogy exists in all cases. The cleavage products of the vegetable proteins are in the main the same as those of animal proteins, but the quantity of each yielded is usually different; for instance, vegetable proteins, as a rule, give a very much higher yield of glutamic acid than do those of animal origin. Further, there are certain vegetable proteins which have hitherto been regarded as peptones, but which do not give the biuret reaction. It seems impossible at present to bring exceptional substances of this kind into any general classification, and the same is true for those curious vegetable proteins, such as gliadin and zein, which stand apart from all other members of the group in being soluble in alcohol.

Emil Fischer's book, which has just been mentioned, will prove a boon to all of those who are grappling with the chemistry of the proteins, for in it are collected his numerous memoirs on the subject down to the end of 1905, together with those published by his colleagues. One searches in vain on the title-page for the legend Vol. I. But it can only be the first of a series, and already there is a goodly supply, mainly from the pen of Abderhalden, for the second. This is just one of the cases, alluded to in the opening paragraph of this report, in which details are being steadily collected. The proteins one by one are being taken to pieces, and the final cleavage products identified and estimated. One cannot but admire the patience of a worker who thus gradually plods through this routine work in order to pave the way to the final generalisation which will come in the future. Much the same sort of thing is being done in relation to the nucleic acids by Levene. The forthcoming index will be a more trustworthy guide to all these numerous papers than any amateur attempt of mine to forestall it. In spite of all the hard work involved in researches of this nature, Abderhalden has found time to write a general Text-Book of Physiological Chemistry, which is a most admirable compendium of up-to-date information, and in its style recalls that of Bunge, Abderhalden's former master. Two new

books have also appeared on the Proteins, each of which has its special merits; the first of these is by Dr. Schryver (Chemistry of the Albumens, J. Murray), and deals mainly with the pure chemistry of the subject. The other, by Dr. Gustav Mann (Chemistry of the Proteids, Macmillan), started as a translation of O. Cohnheim's work, but ended in a volume twice the size of its German prototype. It contains a mine of references to original researches, and is chiefly interesting to those who deal in speculations of a physico-chemical kind.

Globulins.—The distinction between globulins and albumins is one which is mainly based upon differences in solubility; the general reactions of both classes are identical, and the opinion has been freely expressed of recent years that the differences are purely artificial. This idea was first brought into prominence by Starke some years ago, when he showed that by quite simple means the yield of globulin in such fluids as blood-serum can be increased at the expense of the albumin. It was further emphasised by the discovery of certain substances termed pseudo-globulins, which, although they differ from albumins in the readiness by which they can be salted out of solution, nevertheless possess the albumin-like character of being soluble in water. Moll takes much the same view as Starke, and contends, in his most recent paper,¹ that the naturally occurring pseudo-globulin of horses' blood is identical with that prepared artificially from the crystallised albumin of the same blood. Another paper embodying the same notion has been published by Sikes,² in which he shows that, in the absence of bacteria, the globulin of albuminous urine (especially if the fluid is alkaline) increases and the albumin diminishes when the urine is kept.

But in all these cases the test used for the globulins has been that of solubility; there has been no attempt to ascertain whether, when an albumin changes into a supposed globulin, there has been any chemical alteration. When we consider that solutions of albuminous materials are not true solutions, but colloidal solutions, and when we realise that the phenomena of "salting out" are properties that are shared by other colloids, it is not difficult to understand that slight differences of temperature, reaction, and the like will cause a material labelled albumin to undergo small changes of solubility which cause it to be precipitable by reagents which under more normal circumstances precipitate globulins only. The molecules of a protein are unstable ones, and it is possible to imagine further that accompanying the changes of solubility some slight intramolecular changes of a chemical kind may take place

¹ *Beitr. Chem. Physiol. Path.*, 1905, **7**, 311; *Abstr.*, 1906, i, 58.

² *J. Physiol.*, 1905, **33**, 101; *Abstr.*, 1905, ii, 843.

as well. But it is not possible to imagine that any profound chemical change can occur, and there would be a very profound change indeed if an albumin were in very truth transformed into a globulin. For Abderhalden has shown that the proportion of the amino-acid cleavage products in typical globulins differs very considerably from that obtained from typical albumins, and further that the difference is not merely quantitative, but qualitative also; for instance, the albumins do not yield glycine, whereas the globulins do. The difference between albumins and globulins is thus a real and fundamental one. The lessons we should really draw from such work as that of Starke, Moll, and Sikes are, first, that it is unwise to rely on solubility tests in any attempt to distinguish between albumins and globulins, for solubility is a variable quantity; and secondly, that the statement that albumin can be transformed into globulin cannot be accepted unless supported by chemical analysis.

A globulin, then, is a distinct entity, and although Hardy surmises that the globulin of blood-serum is formed by the decomposition of a more complex protein there, he has nevertheless selected it as the substance upon which to perform some very remarkable experiments in his study of colloidal solutions. The paper he has written¹ is a complex and highly technical one. In brief, he shows that globulin is an amphoteric electrolyte, and that globulin salts ionise in solution. If acid is added, the protein molecules assume an electro-positive character, and in the electric field they move towards the cathode; if alkali is added, they assume an electro-negative character and move towards the anode; but in neutral solutions there is no movement, and, moreover, in normal serum "ionic globulin" is absent. The same results have also been obtained by Pauli.² Pauli goes further than Hardy by asking whether the electrical charge of proteins may not possibly explain certain physiological phenomena in connexion with protein chemistry and assimilation, immunity, histological staining reactions, and even fertilisation. It is easier to ask such questions than to answer them. One is on safer ground if one merely records the facts at present, and the main result that a protein may act amphotERICALLY is intelligible if we accept Fischer's view that every protein is a long chain of amino-acids, for every link of the chain is capable of acting either as a base or an acid according as its acidic or basic groups are called into play.

In connexion with Hardy's work, the paper that follows it by

¹ *J. Physiol.*, 1905, **33**, 251; *Abstr.*, 1906, i, 121.

² *Beitr. chem. Physiol. Path.*, 1906, **7**, 531; *Abstr.*, 1906, ii, 180; *Naturw. Rundsch.*, **21**, 3, 17; *Abstr.*, 1906, i, 545.

Mellanby¹ should be read. This also emanates from Cambridge, and deals with globulins; the treatment of the subject is on rather different lines, but is based on physico-chemical conceptions.

Ash Constituents of Protein.—The only other physical paper to which I shall allude is rather an important one by Bayliss.² I gave a very full abstract of it at the time it appeared, and so it will only be necessary here to refer to its physiological side. The ash constituents of proteins have always been somewhat of a puzzle, but Bayliss appears to have obtained the correct solution of the problem. They are not in chemical combination; they are not merely in mechanical admixture, but they are in a condition midway between these two extremes, and are *adsorbed* in the same way that many dyes are adsorbed by fabrics. The main experiments were made with gelatin, and the curve of electrical conductivity of successive distilled water extracts of gelatin is, as in the case of dyes, a hyperbola. Such a curve only approaches the axis (that is, zero concentration) asymptotically, or, in other words, it is impossible to wash out all the electrolytes, except by an infinite number of changes of distilled water, each washing removing a less percentage than the previous one. If such gelatin is again placed in solutions of electrolytes, it again adsorbs them in a non-ionised condition.

Adsorption is doubtless an important factor in many physiological processes. In the staining of histological preparations, the evidence is in favour of the adsorption theory, and here the part played by electrolytes must also be taken into account. If electrolytes are split off from living cells on death or injury, it is clear why such cells readily take up acid dyes; moreover, since electrolytes are unnecessary when the substance to be stained is electro-negative, it is clear why living cells can be stained with basic dyes. The affinity of the Nissl granules of nerve-cells for basic dyes is abolished by previous treatment with neutral salts (Mayr³), and this is also in accordance with Bayliss's results.

It is quite certain that there is no universal law in such matters, and in the staining of cells there are cases of true chemical combination; and such results as those of Macdonald⁴ with injured nerve-fibres and neutral-red are difficult to explain by the adsorption theory; evidently here other factors have to be considered. This is freely admitted by Bayliss, who does not, like so many workers at a new idea, seek to make it explain everything that was obscure before. He certainly puts forward the view that the action be-

¹ *J. Physiol.*, 1905, **33**, 335; *Abstr.*, 1906, i, 122.

² *Biochem. J.*, 1906, **1**, 175; *Abstr.*, 1906, ii, 344.

³ *Beitr. chem. Physiol. Path.*, 1906, **7**, 548; *Abstr.*, 1906, ii, 182.

⁴ *Proc. Physiol. Soc.*, 1905, xxxvii, lxvi; *J. Physiol.*, **32**; *Abstr.*, 1905, ii, 405,

tween toxins and antitoxins is possibly adsorptive, and that the union between an enzyme and a colloidal substrate may be of the same nature, but he does not try to make adsorption explain the universe.

Absorption of Proteins.—Passing from adsorption to absorption, we reach surer ground, and proceed to deal with matters of more practical interest. The old view that proteins are absorbed as peptones and proteoses, and that the fact of these not being discovered in the circulating fluids is due to their being re-synthesised in the cells of the living membrane of the intestine into proteins of the albumin-globulin type, has now been definitely abandoned. Proteins are absorbed as amino-acids, and evidence of any special synthetic formation of proteins by the epithelium of the intestine is lacking (Schryver,¹ Leathes¹); the greater part of these are never built into living protoplasm at all, but they are rapidly converted by the liver cells into urea, and this finds an easy exit from the body by the urine. The small amount that is needed for tissue repair is doubtless picked out of the blood and lymph by the various tissue-cells, and it is there that protein synthesis takes place, just as it is there also where internal respiration occurs. In his early experiments in relation to this problem, Leathes attempted to study it by examining the blood leaving isolated loops of intestine in the interior of which the cleavage products had been placed. The loops were perfused with defibrinated blood, but in these circumstances no absorption whatever occurred, and the intestinal epithelium underwent degenerative changes. Defibrinated blood is not normal blood, and toxic effects have been previously described when it has been used in other experiments (Brodie²). It was therefore necessary to deal with the intact animal, in spite of the greater experimental difficulties of searching for absorbed products when diluted with the whole volume of the blood; and this is what Leathes³ in conjunction with Cathcart has now done. They found that during absorption of protein cleavage products there was no increase in the coagulable proteins of the blood, but that there was a small but distinct rise in the amount of non-protein nitrogen. A superficial observer might ask, Why was the rise only a small one? but the answer is obvious. Absorption is a slow process, and the amount of amino-acids absorbed is diluted with the whole volume of the blood, and further, as soon as it is absorbed, or shortly afterwards, it is removed from the blood. Many years ago Kühne argued that the amount of amino-acids in the intestines at any particular moment during digestion is so small that complete protein cleavage cannot

¹ See last year's *Report*, p. 214.

² *J. Physiol.*, 1900, 26, 48.

³ *Ibid.*, 1906, 33, 462; *Abstr.*, 1906, ii, 181.

be considered to occur to any great extent. He lost sight of the fact that the amino-acids in the intestine were not formed for the purpose of accumulating there, but for absorption. So with amino-acids in the blood, they are not absorbed in order to be stored in that fluid, but are removed from it by the tissue-cells and dealt with there, being either assimilated into protoplasm, or changed and at last discharged as waste material by the kidney. Since then Howell¹ has, by a somewhat different method, been successful also in isolating the amino-acids of the blood, especially after feeding; smaller quantities of them are also present in the lymph.

The Amount of Protein in Diet.—We are thus led in logical sequence again to consider the important practical question of the normal daily requirements of a man in so far as the protein in his food is concerned. As is well known, it is Prof. Chittenden of Yale who is mainly responsible for raising the question, and whilst all sympathise with him in his crusade in favour of temperance in food as well as in drink, and many may confess that in the past they have sinned and eaten too much, it is not surprising that his extreme views have been seriously challenged, and that many are asking now, would it not be equally unwise to eat too little? In deciding whether the Chittenden diet is one which falls under that description, there is a great deal more to be done in the way of accumulating data and performing experiments before any decisive answer can be given. Here experiments on animals are not very conclusive, for if the vegetarian can point to the ox as an instance of a strong beast which thrives on diluted protein nutriment, the meat eater can immediately point to the lion as another vigorous animal who derives his strength from a richly albuminous diet. It is not, however, such a long way from the Japanese to the average European, and here accurate data are sadly needed. We do know that since the Westernising of Japan has commenced, the diet of that country has altered also, and the recent prowess of the Japanese has been, in fact, accounted for by those who know the country by the more liberal supply of nitrogenous food which they now ingest.

At the meeting of the British Association last summer at York, the physiologists and economists combined to discuss this matter, and at the Toronto meeting of the British Medical Association in August, the physiologists united with the doctors in a most interesting debate on the same subject. At the last-named meeting we had the advantage of listening to Prof. Chittenden himself, and although he was ably supported by Dr. Folin, the majority of the

¹ *Amer. J. Physiol.*, 1906, 17, 273.

speakers were against his views, and doubted whether the *minimum* was also the *optimum*.

As an instance of the kind of experimental work which is still necessary, we may take that performed by seven physiologists at University College, London.¹ They took their ordinary diet, and estimated the nitrogen of their urine. The total nitrogen excreted varied from 9·6 to 16·5 grams daily, and, speaking generally, the heavier men excreted most. The influence of body weight as a factor is one which is often lost sight of, and Chittenden himself is not a heavy person. The relation of uric acid to this was found to be comparatively very constant, although that is somewhat of a side issue. Taking the nitrogen excreted as a measure of the protein ingested, the average intake of the seven physiologists would be 93 grams daily, an amount not much below the usual Voit dietary. Atwater's standard is 125 grams daily, and in workhouses and prisons it varies from 134 to 177 grams (see Rowntree's *Poverty, a Study in Town Life*). But the last-named figures are reckoned from bought food, and so the comparison is not quite fair, for the amount of waste is usually considerable in public institutions.

Let us now turn to the question of why the minimum is not also the optimum. Nature, as a rule, does not work in minimums, and Leathes puts it very well in his book when he says it is not considered unphysiological to take a diet which will yield more than the minimum of faecal refuse, and he calculates that the diet provided for an infant by nature in the shape of milk is, even allowing for growth, ten times richer in protein than the requirements of its endogenous protein metabolism would make apparently necessary.

There is probably a real need for an excess of protein beyond the apparent minimum. In diamond mining a large quantity of the blue earth of Kimberley must be crushed to obtain the precious stones. It probably is the case that among the many cleavage products of protein the majority may be compared to this waste earth, and we get rid of them as quickly as possible in the excretions, but some few may be unusually precious for protein synthesis in the body, and that in order to get an adequate supply of these, a comparatively large amount of protein must be ingested. It does seem as though the large size of the liver (the riddle of the body, as Leathes terms it) is for the express purpose of dealing with the large amount of nitrogenous waste, much as the great capacity of the rectum enables the body to grapple with a large amount of faecal refuse.

Such arguments are of more value than those so often used by

¹ *Proc. Physiol. Soc.*, 1906, x; *J. Physiol.*, 34; *Abstr.*, 1906, ii, 463.

physicians when they say that the intake of protein is for the purpose of supplying the body with "reserve force." Reserve force is just one of those phrases that sound so satisfactory, but which it is very difficult to define. In the case of carbohydrates, we have a reserve force in the shape of a storage of glycogen; in the case of the fats, the same is true, and the reserve is stored in the adipose tissue, but we know little or nothing of a storehouse for protein, for the amount ingested is usually dealt with and disposed of within a few hours after it is taken into the body. Pflüger and his pupil W. Seitz¹ have, it is true, suggested that the liver is a storehouse, not only for carbohydrates, but for proteins also, and have supported their views by observations, partly chemical, partly histological, on starved and fed animals, but the idea has not at present met with universal acceptance. Others have supposed that protein storage may occur in the muscles, at any rate in some animals. Be that as it may, the term reserve force is not one to be wholly scoffed at; it is not entirely meaningless, and it is after all an undoubted factor in the resistance of the body to fatigue and disease. It is a matter of common observation how much different people vary in "stamina," as it is sometimes called. This, in part, depends on the condition of the leucocytes or phagocytes, in part on the opsonic power of the blood-plasma, and in part on other factors less fully understood. It may be that the fresh supply of protein stimulates and activates such protective mechanisms in the body, and certainly it is a practical fact that good feeding enables the body (as in tuberculosis) to repel and neutralise the deleterious agents which produce disease. Each leucocyte may every day undergo very slight wear and tear, but it will be more likely to receive the "stitch in time" if an abundant supply of repairing material is in its neighbourhood.

Some kind of attempt has already been made to work out the idea as to which of the Bausteine (to use the German phrase) of the protein molecule are so specially valuable for the synthesis of protein. The vegetable proteins do not appear to be so nutritious, to use the popular phrase, as those of animal origin, and this does not seem to be wholly due to the fact that they are not so readily digestible. For are the vegetable proteins after all the same as the animal ones? Work on their Bausteine seems to answer no when we consider, for instance, their high yield (often over 30 per cent.) of glutamic acid. The same note is also struck by two Baltimore physicians (Lewellys Barker and B. A. Cohoe)²; they point out that certain articles of diet will "agree" and others

¹ *Pflüger's Archiv*, 1906, **111**, 309; *Abstr.*, 1906, ii, 241.

² *J. Biol. Chem.*, 1906, **1**, 229; *Abstr.*, 1906, ii, 102.

"disagree" with people. On the supposition that this may be due to the distribution of the nitrogen, they made determinations of mono-amino-nitrogen, di-amino-nitrogen, &c., in various foods (veal, pork, sirloin, chicken, fish, &c.), and have given their results in tables. The differences are very striking, but their ultimate valuation is for the future. Still, this again is the sort of work which must be done before our knowledge can be based on the bed-rock of experiment.

At present we can therefore only make a rough guess as to which of the Bausteine are the diamonds; but it does appear as though phenylalanine and its near relative tyrosine were such; they are comparatively scanty, and it is known that on injection into the blood stream they do not reappear as urea in the urine. We further know that proteins which yield no tyrosine, such as gelatin, are of inferior value as food. Gelatin is also destitute of the tryptophan radicle, so perhaps tryptophan is particularly useful too; and if tyrosine and tryptophan are added to a gelatin diet, the animals fed on it thrive better than those whose sole nitrogenous food is gelatin only.¹ Histidine and pyrrolidine have been also suggested as being in the same category, but there again we must await further information.

A critical examination of Chittenden's experiments and conclusions has recently issued from the pen of F. G. Benedict.² Benedict's training in the Atwater laboratory would naturally prejudice him against a revolutionary doctrine; still, his objections are serious, and will have to be refuted before Chittenden and his comrades can urge their case successfully. But there are other subjects that press for consideration, and so I will be content with referring readers to the abstract I recently supplied to the *Journal*, or still better to the original paper, which will amply repay perusal by those interested in the subject.

Protein Decomposition Products. Amino-acids.—Some interest has centred round the question whether amino-acids occur in normal urine, and the introduction of naphthalenesulphonic chloride as a reagent for their detection has rendered such an investigation feasible. It seems to have been established that a minute amount of glycine and possibly of some other amino-acids is normally present (Embden and Reese,³ A. Lipstein,⁴ G. Forssner,⁵ Abderhalden

¹ Similar experiments have been made on young animals by Hopkins and Miss Willcock (*J. Physiol.*, 1906, **35**, 88), in relation to the maize protein called zein. Zein contains no tryptophan. Zein *plus* tryptophan maintains growth.

² *Amer. J. Physiol.*, 1906, **16**, 409; *Abstr.*, 1906, ii, 689.

³ *Beitr. chem. Physiol. Path.*, 1905, **7**, 411; *Abstr.*, 1906, ii, 108.

⁴ *Ibid.*, 327; *Abstr.*, 1906, ii, 109.

⁵ *Zeit. physiol. Chem.*, 1906, **47**, 15; *Abstr.*, 1906, ii, 243.

and Schittenhelm,¹ F. Samuely,² Wohlgemuth and Neuberg³), but whether this has any physiological significance is uncertain; the view expressed by the majority of observers is that the amount is really a negligible quantity. The importance of the inquiry arises from the study of pathological urine. If, for instance, the amount is increased in gout, we should be provided with another step in the ladder of knowledge concerning what is still an obscure disorder. Here, unfortunately, the observers disagree, some describing an increase in gout, leucæmia, and pneumonia, but others stating that the variations are within normal limits.

A still more wide-reaching inquiry concerning the fate of amino-acids in the body is that which has been undertaken by Dakin.⁴ It may be taken as pretty well proved that protein matter in the body yields carbohydrate, quite apart from the glucosamine which in some proteins is contained as a prosthetic group. Certain amino-acids, of which alanine is the one that has yielded the most positive results, are after administration converted into either glycogen in the liver or sugar in the urine. The substitution of hydroxyl for the amino-group in alanine will give us lactic acid, and lactic acid is readily formed from sugar, and so it is probable that the opposite change from lactic acid to sugar may also occur. This, however, is only one possibility, and certainly the more intimate chemistry of such reactions is still a matter of hypothesis only, and is difficult to explain. Lang has shown that enzymes are present in the liver which remove ammonia from amino-acids, and Dakin considers that ferment activity will also explain the removal of carbon dioxide from their carboxyl group, as in the transformation of ornithine into tetramethylenediamine. Now if both ammonia and carbon dioxide are removed from an amino-acid, an alkyl group rich in carbon is left, which might be further transformed into carbohydrate, or into carbon dioxide and water. Dakin selected a method which closely approximates a biochemical reaction, namely, Fenton's method of oxidation by means of hydrogen peroxide and a trace of a catalyst such as ferrous sulphate⁵; the amino-acids selected for experiment were glycine, alanine, and leucine. All of these may be represented by the formula $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$, where R is either a

¹ *Zeit. physiol. Chem.*, 1906, **47**, 339; *Abstr.*, 1906, ii, 470.

² *Ibid.*, 376; *Abstr.*, 1906, ii, 470.

³ *Med. Klin.*, 1906, No. 6; *Abstr.*, 1906, ii, 874.

⁴ *J. Biol. Chem.*, 1906, **1**, 171; *Abstr.*, 1906, ii, 105.

⁵ The same method has been adopted by Battelli and Stern (*Compt. rend.*, 1905, **141**, 916; **142**, 175; *Abstr.*, 1906, ii, 107, 184) in their investigations of oxidations in tissues and tissue extracts. The place of the ferrous salt is in the body taken by what they term anti-catalase, and this disappears soon after death. Lactic, acetic, and formic acids are decomposed and carbon dioxide evolved. The method does not oxidise urea, and urea is also the chief nitrogenous end-product in the body.

hydrogen atom as in glycine, or a methyl or *isobutyl* group (as in alanine and leucine respectively). On oxidation all are readily resolved at the ordinary temperature into carbon dioxide, ammonia, and an aldehyde. In the case of glycine, the aldehyde produced is formaldehyde, and this is the substance which is obtained photosynthetically in plant life, and is there the undoubted forerunner of carbohydrate, into which it is transformed by condensation, a process which has been successfully imitated in the laboratory by Butleroff and Fischer. It was, however, found that the yield of aldehyde was less in the case of glycine than in that of alanine or leucine; this is because it is partly oxidised into formic and glyoxylic acids. The formation of glyoxylic acid is not without interest, as this acid occurs in unripe fruit, and on ripening is converted into sugar.

In similar fashion, alanine yields acetaldehyde and acetic acid (but not pyruvic acid, the acid corresponding with glyoxylic acid), whilst leucine yields *isovaleraldehyde* and *isovaleric acid*.

I think all chemists will agree that this research marks an important advance, and one that should lead investigators onward. It is not until chemists are able to repeat vital processes, by methods that they understand, that they can hope to comprehend what is occurring in the hidden laboratory of the living cell. Not the least striking of the conditions of Dakin's experiments is that they occurred at the ordinary temperature.

Glyoxylic Acid.—The possibility that this substance is a product of metabolism is shadowed in Dakin's work, and is shown to be a probability in a later paper by the same worker.¹ He was not, however, the first in this particular field, for Almagia and his colleagues Pfeiffer and Inada² had previously suggested that it is a decomposition product of uric acid, and found it in the urine, especially of people suffering from gout. In herbivora fed on hay it is also present, and is derived there from the aromatic substances in the food. It cannot, however, be said that the test adopted for the detection of glyoxylic acid in urine is a very convincing one. Hopkins and Cole showed that the so-called Adamkiewicz reaction for proteins depends for its occurrence (1) on the presence of the tryptophan group in the protein, and (2) on the presence of an impurity (glyoxylic acid) in the glacial acetic acid employed. Eppinger³ had the brilliant idea that not only may glyoxylic acid be used as a test for tryptophan, but that tryptophan may also be used as a test for glyoxylic acid. Subsequent observers, however (for

¹ *J. Biol. Chem.*, 1906, **1**, 271; *Abstr.*, 1906, ii, 374.

² *Beitr. chem. Physiol. Path.*, 1905, **7**, 459, 466, 473; *Abstr.*, 1906, ii, 109.

³ *Ibid.*, 1905, **6**, 492; *Abstr.*, 1905, ii, 543.

instance, Dakin,¹ Schloss²), have pointed out that this does not necessarily follow, and regard the test as untrustworthy, because tryptophan may give the same coloration with other substances also.

Schloss has introduced a modification of the Eppinger test, but whether this is more satisfactory remains to be proved. Eppinger stated that the administration of various substances (alcohol, glycine, glycolic acid, sarcosine, betaine, &c.), led to the appearance of the acid in the urine, but this Schloss could not confirm. He only obtained a positive result when allantoin was given, and this is by no means an unimportant result in view of Almagia's theory of the relationship of glyoxylic acid to uric acid metabolism. Schloss further examined the organs of the body, and believes that glyoxylic acid when formed is destroyed in the body, especially in the liver and brain.

Whether glyoxylic acid is concerned at all in the Adamkiewicz reaction appears questionable when one considers some results recently published by Rosenheim.³ He quite agrees with Hopkins and Cole in regarding the reaction as due to the presence of the tryptophan (indole) group in the protein molecule. But he obtains what appears to be an identical reaction both to the naked eye and to the spectroscope when formaldehyde is added to a protein solution in the presence of sulphuric acid containing oxidising agents. According to this view the impurity in glacial acetic acid responsible for the colour is not glyoxylic acid, but formaldehyde, and the presence of impurities in the sulphuric acid (for instance, nitrous acid, ferrous salts) is also necessary; these produce diformaldehyde-peroxide hydrate, and this reagent gives the test in the presence of protein and pure sulphuric acid. I understand, however, from Dr. Hopkins that he is prepared to defend his original views, and there we must leave the question for the present; but until it is settled, the search for glyoxylic acid by means of tryptophan must be suspended.

Lactic Acid in Intermediary Metabolism.—I mentioned lactic acid just now as a possible intermediary between alanine and sugar in the body. The whole question of the meaning of lactic acid is not only fraught with interest, but also surrounded with great difficulties. Its close relationship to sugar is undoubted, whether we are concerned with the building up or the breaking down of sugar molecules in metabolism, and yet the idea is gaining ground that the most important variety of lactic acid found in the body (dextrorotatory or sarco-lactic acid) has a protein origin, by way of such amino-acids

¹ *Loc. cit.*

² *Beitr. chem. Physiol. Path.*, 1906, **8**, 445; *Abstr.*, 1906, ii, 785.

³ *Biochem. J.*, 1906, **1**, 233; *Abstr.*, 1906, ii, 508.

as alanine, and its compounds phenylalanine and tyrosine. G. Lusk and A. R. Mandel¹ found that lactic acid disappears from both blood and urine in phosphorus poisoning, when phloridzin glycosuria is induced. This indicates that lactic acid produced from protein (whether in liver, intestinal wall, or elsewhere) is first synthesised to sugar within the body before further distribution to the tissues occurs. In phosphorus poisoning this is followed by cleavage and a second production of lactic acid. But when diabetes is present, and when the mammary glands are utilising dextrose to form lactose, then the cells affected become "sugar hungry," and also attract fat in greater quantity than they can burn it, and so fatty degeneration, which is really fatty infiltration, is seen. In the diabetic organism there is therefore a complete conversion of *D*-lactic acid into dextrose, and the same is true partially for *i*-lactic acid.

The difficulties of the lactic acid question have led observers in the past into curious mistakes; the convulsions of puerperal eclampsia have, for instance, been attributed to the presence of the acid in the blood and cerebrospinal fluid.² The acid is there, but it is obviously and undoubtedly the consequence and not the cause of the convulsions.

Ferments.

There is nothing very new or very striking to mention in relation to work on enzymes during the last year. It is becoming more and more certain that these agents act as catalysts in increasing the velocity of chemical reactions.³ A succinct and very readable account of this modern view of ferment action has been written by Bayliss, and published in Mr. Murray's new review, *Science Progress*.⁴ There are, of course, certain differences between enzymes and the inorganic catalysts (for instance, their destruction by a high temperature), but, as Bayliss points out, these are all explicable on the hypothesis that the former are colloidal substances.

In addition to the papers of Armstrong which have been already mentioned, there have been others on what one may term isolated points, such as the velocity of action of trypsin,⁵ the supposed identity of rennin and pepsin,⁶ the decomposition of caseinogen by

¹ *Amer. J. Physiol.*, 1906, **16**, 129; *Abstr.*, 1906, ii, 463.

² This view is not altogether confined to the past, but has again been urged by several investigators during the present year (Zweifel, *Münch. med. Woch.*, 1906, **53**, 297; Füh and Lockeman, *Centr. Gynaek.*, 1906, **41**; *Abstr.*, 1906, ii, 472.

³ See, for instance, Neilson, *Amer. J. Physiol.*, 1906, **15**, 148; *Abstr.*, 1906, i, 125.

⁴ Oct., 1906, 281.

⁵ Hedin, *J. Physiol.*, 1906, **34**, 370; *Abstr.*, 1906, ii, 780. See also same author on Anti-trypsin, *Biochem. J.*, 1906, **1**, 474, 484; *Abstr.*, 1906, ii, 780.

⁶ Sawjaloff, *Zeit. physiol. Chem.*, 1905, **46**, 307; *Abstr.*, 1906, ii, 98.

trypsin and alkalis,¹ all of which are interesting in themselves, but do not lend themselves to a general discussion.

In reference to co-ferments, it is apparently becoming established that these are, as hinted in last year's report, of a simple and stable nature, being, in some cases at any rate, inorganic in nature. In this relation the papers by Delezenne² on the activation of pancreatic juice by calcium salts, by Harden and Young³ on the alcoholic fermentation in which the presence of phosphates will partly, but certainly not entirely, explain the favouring action of boiled yeast juice, and by Loevenhart,⁴ in which Magnus's co-ferment of lipase is shown to consist of bile salts, should be read.

Plimmer's paper on the adaptation of the pancreas to lactose⁵ does, however, raise a general question. The idea that the organism is able to adapt its secretions to the calls made upon it originated from the brilliant and suggestive work of Pawloff, and one of the most remarkable of these adjustments was described by Weinland and later by Bainbridge; they stated that in animals which received no milk in their food, no lactase was secreted by the pancreas; but the administration of milk or lactose to the animals educated the pancreas to secrete the ferment necessary for the hydrolytic cleavage of milk sugar. Plimmer has now shown that this result was due to fallacious methods of experiment and analysis, and that this supposed adaptation does not really occur. This has certainly not killed the notion of adaptation,⁶ but it has removed from it a very important pillar of support, and this naturally leads one to hesitate before accepting other proofs, and to demand that the experiments be repeated with more rigorous controls.⁷

Cleavage of Peptides by Enzymes.—This is also another important general question, although it is early days yet to attempt any generalisation. The peptides are numerous, and enzymes are numerous, and to work out all the possible combinations and permutations will take time; and this is the Herculean task Fischer, Abderhalden, and their colleagues⁸ have started. Some of the peptides

¹ Bayliss and Plimmer (*J. Physiol.*, 1906, **33**, 439; *Abstr.*, 1906, i, 325.

² *Compt. rend.*, 1905, **141**, 751, 914; *Abstr.*, 1906, ii, 99, 100.

³ *Proc. Roy. Soc.*, 1906, **77**, B, 405; *Abstr.*, 1906, i, 470.

⁴ *Proc. Amer. Physiol. Soc.*, 1905, xxvii; *Amer. J. Physiol.*, **15**; *Abstr.*, 1906, i, 328.

⁵ *J. Physiol.*, 1906, **34**, 93; *Abstr.*, 1906, ii, 239.

⁶ There are, for instance, papers still being published in relation to it; see "Adaptation of the Salivary Secretion," by Neilson and Terry (*Amer. J. Physiol.*, 1906, **15**, 406; *Abstr.*, 1906, ii, 238).

⁷ A more recent paper by Plimmer (*J. Physiol.*, 1906, **35**, 20) has already adduced evidence that other cases of supposed adaptation have no foundation in fact.

⁸ Some of the most important papers in the series are as follow: *Zeit. physiol. Chem.*, 1905, **46**, 52; 1906, **47**, 346, 359, 391, 466 (*Abstr.*, 1906, ii, 99, 462, 464).

undergo cleavage, some do not, and others are broken up only by certain enzymes. For instance, glycyl-*l*-tyrosine is readily decomposed into its constituents by trypsin, but not by pepsin-hydrochloric acid; such an observation furnishes us with a distinguishing character of these two enzymes which has for so long been lacking. Glycylglycine is not split by pancreatic juice, but it is by liver extract. Such an observation started Abderhalden on the track of examining the action of various tissue extracts, and there is no doubt that a knowledge of the part played by these tissue enzymes will teach us a great deal about intermediary metabolism. Enzymes have in many cases been known to exhibit a "reversible action," and so it is quite possible that the same ferments which split peptides may also, when acting the other way round, contribute to the synthesis of proteins in the tissue cells. No evidence of reversible action has, however, been forthcoming in the experiments hitherto performed *in vitro*.¹

Studies of this nature, and studies on autolysis, have established the importance of the tissue enzymes; we now know that ferments which produce hydrolysis are not confined to the interior of the alimentary canal, but that most of the body cells are provided with ferments of most diverse kinds, which assist them either in utilising the nutrient materials brought to them by the blood stream, or in breaking them down previous to expelling them as waste substances. Claude Bernard, when he discovered the ferment which enables the liver cells to transform glycogen into sugar, little foresaw that this was the first of a long series which were to be discovered many years later. Among such later discoveries we may mention tissue erepsin and arginase.

But the best instance of all is seen in the formation of uric acid from nuclein; in this case we have to deal with numerous ferments acting in succession. Thanks to Walter Jones in America and Schittenhelm² in Germany, our knowledge on this question is pretty complete. The two observers have indulged in a certain amount of polemics, but those who are outside the controversy will rejoice that, after all, on the main questions involved there is agreement. The first ferment to come into play is *nuclease*, and this liberates the nuclein bases. This ferment is found in pancreatic juice, but it is not identical with trypsin; in fact, it is destroyed by tryptic action (Sachs³); it is, however, also found in the extracts of many tissues, and so the work started in the intestine is finished by the tissue cells.

¹ Abderhalden and Rona (*Zeit. physiol. Chem.*, 1906, **49**, 31; *Abstr.*, 1906, ii, 873).

² Jones and Austrian (*Zeit. physiol. Chem.*, 1906, **48**, 110; *Abstr.*, 1906, ii, 561); Schittenhelm and Abderhalden (*ibid.*, **47**, 452; *Abstr.*, 1906, ii, 465). For previous paper, see last year's *Report*.

³ *Zeit. physiol. Chem.*, 1905, **46**, 337; *Abstr.*, 1906, i, 126.

The next ferments which act remove the amino-group from the purine bases that contain it; thus adenine ($C_5H_5N_4 \cdot NH_2$) is converted by *adenase* into hypoxanthine ($C_5H_4ON_4$) and guanine ($C_5H_3ON_4 \cdot NH_2$) is converted by *guanase* into xanthine ($C_5H_4O_2N_4$). Finally, *oxydases* step in and oxidise hypoxanthine into xanthine, and xanthine into uric acid ($C_5H_4O_3N_4$). By examining extracts of various organs, the distribution of these numerous ferments is found to vary somewhat in different animals, although in general the spleen and the liver are the organs where they are most abundant. But the examination of such extracts has shown in addition that the long list is not yet complete, for some extracts in part break up the uric acid which has been formed into simpler substances,¹ and the ferment which destroys uric acid is called the *uricolytic* ferment.² We therefore learn that the uric acid discharged in the urine is only the balance left over when the amount destroyed is deducted from the amount originally formed. In other words, the body possesses to some extent the power of protecting itself from an excessive formation of uric acid, and so from the evils which would result from an accumulation of this substance.

The Secretion of Urine.

Bowman was the first to put forward the hypothesis that the formation of urine is a double process; the glomeruli consist of blood vessels in which there is high pressure, and consequently they have been looked on as a filtering apparatus where water and certain soluble salts escape. The convoluted tubules with their secretory epithelium are the parts of the apparatus where urea and other organic substances are added to the glomerular flow. The secreting cells are able to pick out the urea, mainly formed in the liver, from the blood, and transfer it to the urine.

Ludwig, on the other hand, considered that practically all the urinary constituents found an exit from the blood at the glomeruli, and that the function of the tubules was to reabsorb some of the water and so increase the concentration of the urine. This view has been supported by the recent work of Cushny, who has put forward evidence that reabsorption of water, and to a certain extent of some salts, occurs in the tubules. The whole tendency of modern research, however, apart from Cushny's work, has been to confirm the original statements of Bowman, and to prove the tubules to have as their principal function secretion and not absorption.

¹ See also the papers by Almagia and his colleagues already quoted.

² The fact that uric acid is destroyed is no new discovery, however. See, for instance, H. Wiener (*Arch. exp. Path. Pharm.*, 1899, 42, 374; *Abstr.*, 1900, ii, 153).

The work of Brodie and Cullis¹ is a very important piece of research from this point of view. They found, in a dog in which diuresis was produced by sodium sulphate, that the volume of urine secreted by one kidney which was working against a small ureter pressure was greater than that formed by the other kidney which served as a control; the volume of sulphate secreted on the obstructed side was also usually in excess. A saline diuretic excites the cells to greater secretory activity, and does not work solely by causing changes in the blood and in the circulation. Nevertheless, it was necessary in such experiments to exclude any artificial changes in the blood flow through the kidney, and this was done by making the ureter pressure sufficiently small. If phloridzin was employed, the volume both of the urine and the sugar was greater on the obstructed side. Such results negative Ludwig's view of kidney action, for an increased pressure in the ureter would promote absorption if Ludwig's theory is true; they indicate that the glomeruli will excrete more water and probably more salt, and that the tubules excrete more salt when excited by a small ureter pressure.

Heidenhain's old experiment with indigo, in which he showed that the tubules and not the glomeruli are the places where the excretion of this foreign substance occurs, has recently been repeated by Basler.² This observer further introduced the indigo into the kidney calyces, but could not find that it was reabsorbed by the living cells of the tubules, although some ultimately diffuses backwards into the lumen of the tubules. But if the same experiment was performed with sodium ferrocyanide, this salt was shortly afterwards excreted by the other kidney. This certainly shows that absorption of the salt had occurred, but it does not prove that the cells of the tubules had been instrumental in the absorption; it rather appears that the salt had simply diffused into the lymph vessels or blood vessels in the neighbourhood of the injection.

The mammalian kidney presents much greater difficulties to the experimenter than the kidney of the frog; and Nussbaum, who followed in Bowman's footsteps, utilised the fact that the glomeruli in the latter animal are supplied with blood by the renal artery and the tubules by a different vessel, namely, the renal-portal vein, in his classical experiments by which he sought to unravel the part played by the two mechanisms. Nussbaum's anatomical facts are undoubtedly true, and there is no anastomosis between the two sets of blood vessels; if all the branches of the renal artery are tied, the glomeruli are rendered absolutely bloodless; Bainbridge and Beddard³ showed, how-

¹ *J. Physiol.*, 1906, **34**, 224; *Abstr.*, 1906, ii, 468.

² *Pflüger's Archiv*, 1906, **112**, 203; *Abstr.*, 1906, ii, 468.

³ *Proc. Physiol. Soc.*, 1906, ix, *J. Physiol.*, **34**; *Abstr.*, 1906, ii, 469; *Biochem. J.*, 1906, **1**, 255; *Abstr.*, 1906, ii, 563.

ever, that under these conditions, although the tubules are still receiving blood, the kidney absolutely refuses to work at all; for the blood they receive is venous blood, and the loss of an arterial supply asphyxiates the kidney and leads to death and desquamation of the renal epithelium. This may be obviated by placing the frog in nearly pure oxygen at atmospheric pressure, and a secretion of urine follows the injection of urea, dextrose, phloridzin, or disodium hydrogen phosphate.

Experiments on artificial perfusion lead also to similar results (Miss Cullis¹). By quite simple operations, an arterial perfusion (by way of the renal artery to glomeruli), a venous perfusion (by way of renal portal vein to tubules), or both (that is, a total perfusion), may be obtained; and the necessary oxygen supply is kept up by means of oxygenated saline solution (Locke's fluid). Various diuretics were added to the perfusing fluid, and their effects noted. Phloridzin was found to excite the tubule cells directly; they form dextrose and discharge it into the urine. Caffeine also excites the same cells, although it also probably has a slight similar action on the glomerular epithelium. With sodium sulphate, no flow of urine occurs unless the circulation through the glomeruli is maintained, and other saline diuretics act in the same way. Dextrose acts mainly on the glomeruli, but to a small extent on the tubules. Both glomeruli and tubules are concerned in the elimination of urea, but there were some difficulties in determining the relative importance of the two, for strong solutions of urea kill the cells. Again, as in the dog, analysis of the urine showed no evidence of reabsorption in the tubules.

Such experiments undoubtedly prove the power of secretion which the cells of the tubules possess. They do more than this; they show that the old idea that the glomerular apparatus is a passive filter is incorrect, but that the cells that cover it, thin though they are, are nevertheless secretory also. At the meeting of the British Association in Toronto, Brodie advanced the view that the high blood pressure in the glomeruli is not to promote filtration at all, but to enable the glomerular tuft at the commencement of each renal tube to act as a sort of force pump to assist in driving the urine to its destination. Basler has also called attention to the high resistance the glomerular outflow has to overcome in the narrower portions of the tubule, as, for instance, in the loop of Henle. Whether this new idea will ultimately prevail it is at present impossible to prophesy. Bainbridge and Beddard, who concur in regarding the glomerular epithelium as secretory, also suggest the presence of secretory nerves; nerve endings have been found by Berkeley in the renal epithelium, and it is difficult to explain diuresis following injury to the central nervous system without assuming that these act as secretory nerves.

¹ *J. Physiol.*, 1906, **34**, 250; *Abstr.*, 1906, ii, 468.

An interesting outcome of such studies is a calculation of the work which the kidney does. The kidney cannot be doing more work than its metabolism accounts for. If we suppose the kidney lives on its protein (and the figures would not be very different if we supposed it lives on carbohydrate), we start with the following constants:—1 c.c. of oxygen oxidises 1 milligram of protein, and forms water, carbon dioxide, and urea (Barcroft and Brodie¹); in doing so it gives out 4 large calories, to adopt Rübner's figure for the physiological heat value of albumin. In a certain experiment the oxygen used by the kidney was 4 c.c. per minute; this was equivalent to 16 calories, or to 680,000 gram-centimetres of work, and the energy transformed from potential to kinetic cannot have been less than that. What evidence is there of mechanical work as an offset against this? One way in which the work manifests itself is in the concentration of the urine. The urine in regard to its various constituents is many times more concentrated than the fluid of the blood, and from freezing-point determinations it was found that 14,700 gram-centimetres of work were done in this way in the example just taken. No doubt if the calculation took into account each salt separately, a higher figure than 14,700 would have been obtained, but even then much of the kidney energy is left unaccounted for; we can only suppose that the transference of water itself at a rapid rate through protoplasm is on occasion a process which involves the active metabolism of the cells.

Micro-chemistry.

The number of workers at this instructive and important aspect of biological work is lamentably small. In addition to the paper by E. Mayr already quoted on the influence of salts on the staining and fixation of nerve-tissues, there is only one other of importance that I can find in the year's output. This also deals with nerve-cells and fibres, with special reference to the distribution of chlorides in them (Macallum and Menten²). Macallum has shown previously that the well-known reduction staining with silver nitrate, so much used in histology, is due to the presence of chlorides. The transverse striations produced at the nodes of Ranvier in nerve-fibres, and termed the lines of Frommann, can be obtained at any portion of the axis cylinder, provided means are taken to allow the reagent to get at it. These lines do not indicate, however, a pre-existing distribution of the chlorides in alternating layers. The same appearance can be reproduced in capillary tubes containing egg-white, or gelatin impregnated with potassium dichromate (Boehm, Liesegang). Ostwald explains this by supposing that, when the critical concen-

¹ *J. Physiol.*, 1905, **33**, 52.

² *Proc. Roy. Soc.*, 1906, **77**, B, 165; *Abstr.*, 1906, ii, 182.

tration in the advancing solution is reached, precipitation begins and is continued until a stria is formed. This brings the solution back to the metastable condition; then another development of the labile condition obtains, and thus a new stria after an interstriae zone is formed. As the silver salt becomes more and more dilute, critical concentration is obtained later and later, and so new striae are separated by interstriae zones of increasing width.

The cytoplasm of the nerve cell shows the same appearances, but less intensely; this may be due to difficulty of penetration, but it is held that probably the cell-body is poorer in chlorides than the axon. The nucleus is destitute of chlorides.

The mixture of electrolytes and colloids in the nerve-fibre would not permit the ions carrying the electrical charge to travel unimpeded, and the change of potential transmitted would travel with diminished velocity. This would bring into line the nerve impulse and the action current of nerve. It is freely admitted that caution must be exercised at present in drawing physiological conclusions from physical data, but the following facts are very suggestive:—(1) the presence of electrolytes (chloride or chlorides) in a concentrated degree and uniform in distribution; (2) the maintenance of this concentration through the impermeability of the sheaths of the fibres, and (3) the high conductivity of the axon, and the occurrence of electrical phenomena when it is injured.

Such speculations should be compared with those set forth by Macdonald in papers already referred to.

Receptive Substances.

I started this report with the laudable intention of avoiding, as far as possible, speculative questions, but I find I have again landed myself in the last section in another of those interesting regions where physical chemists and physiologists can meet and argue. In the present state of physiology it is, in fact, impossible to avoid hypothetical matters, and it is quite impossible also to conclude a report of this kind without a reference to Langley's recent suggestions on "receptive substances." The idea seems to form an underlying basis of a good deal of the work that has recently come out of Cambridge,¹ and it has finally found expression in the Croonian lecture which Prof. Langley delivered before the Royal Society.² We may best approach it, as Langley himself does, by a definite example. Nicotine causes prolonged contraction in certain muscles

¹ See, for instance, H. K. Anderson on "The Action of Alkaloids on the Iris" (*J. Physiol.*, 1905, **33**, 414; *Abstr.*, 1906, ii, 104).

² *Proc. Roy. Soc.*, 1906, **78**, B, 170—194. The question is also treated in *J. Physiol.*, 1905, **33**, 374; *Abstr.*, 1906, ii, 111.

of the bird even after their nerves have been cut, or after paralysis has been caused by curare. The nicotine contraction is lessened by a sufficient dose of curare, the two poisons being antagonistic, but nicotine is the more powerful. Degeneration of the motor nerves leaves these effects unaltered, but there is increased responsiveness to nicotine, and the action of curare is less marked. Under these conditions, the axon endings are destroyed, and so the drugs must act on the muscle itself; but as the muscles respond to direct stimulation, the poisons cannot be acting directly on the contractile substance, but on other substances in the muscle, which may be termed "receptive substances." This deduction may be applied to other cases, and the majority of poisons ordinarily supposed to act on nerve-endings probably act on receptive substances in the cells the nerve-endings are distributed to. Adrenaline falls into this category; and secretin, iodothylin, and other internal secretions may also act in the same sort of way, although the cells they stimulate may have no necessary nerve supply.

These and many other speculations arising out of the general idea are propounded, but the original papers must be consulted for these. It will be sufficient for our purpose merely to state what the general hypothesis is.

It is postulated that in all cell-protoplasm two constituents at least are present: (1) a chief substance concerned with cell function, and (2) receptive substances which may be acted on by chemical materials, or in certain cases by nervous stimuli. The receptive substance affects, or can affect, the metabolism of the chief substance. A cell, for instance, can make motor or inhibitory receptive substances, or both, and the effect of a nerve impulse will then depend on the proportion of the two kinds of receptive substance which is affected by the impulse.

It is quite impossible to criticise such a theory at present, for criticism, like the main theory, must be supported by experiment. All one can say is that the theory is an exceedingly attractive one, and one which does explain some of our present difficulties.

Previous to the appearance of this new idea, physiologists were agreed that there are only two possible ways in which a nerve impulse can fire off such a structure as a muscular fibre, with which its ending is in contact. One of these ways is an electrical one, the other a chemical one. The electrical theory is known as the "discharge hypothesis," and, put in the briefest possible way, it assumes that the stimulus to muscular action is the current of action in the nerve terminal. Electro-physiologists have been fairly successful in explaining away most of the objections which have been raised against the "discharge-hypothesis," but they have never, to my mind, succeeded in solving what is the greatest difficulty of all, and

that is the mystery of inhibition. An action current, feeble though it is, is still a conceivable agent in rendering another tissue active. It is most difficult to understand how it can succeed in rendering another tissue inactive, as, for instance, the *vagus* does the heart. An attempt has been made to explain the phenomenon of inhibition by assuming differences in shape in the nerve-endings; in the ordinary motor nerve terminal it has been supposed that the effect at the entrance of the fibre, a spot which plays the part of the cathode of the terminal, is most concentrated, because the entering point is a small one, whereas the anode consists of a number of widely-distributed points in the final branchings of the axon, and so the anelectrotonic or depressing effect is more diffused, and therefore not so effective. On the other hand, the end organ of an inhibitory fibre is assumed to be pear-shaped; the base of the pear is at the entering of the fibre; the end organ then narrows off to a stalk, the end of which is the anode; the anode being then a smaller point than the wide cathode, anelectrotonic effects are more concentrated, and so more effective; in fact, sufficiently so to overcome any stimulating effect the cathode would have. There is, however, very little histological evidence, and certainly not convincing evidence, that inhibitory nerve-endings have such a shape as the theory demands.

Langley's new hypothesis appears to be the first workable one in favour of the view that a nerve acts as a stimulus by producing chemical changes, and it is certainly easier to understand opposite chemical changes, or the reversal of a chemical change, than to imagine opposite electrical effects produced by differences in the shape of the nerve-ending. If, however, a muscle is rendered active by the production of a chemical material that plays the part of a stimulus, and if it is rendered inactive by the production of chemical changes in the opposite direction, we really only throw the main difficulty further back; for we have still to ask how is it that the nervous impulses produce these chemical effects on the receptive substance or substances? Even if the presence and importance of these receptive substances, or intermediaries, between nerve and muscle be admitted, it may be still necessary to call to our assistance the "discharge hypothesis," or some variation of it, to explain how the nerve affects the intermediary material.

W. E. Dixon¹ has already brought forward evidence that chemical substances are produced in the heart when it is inhibited, and that

¹ Communication to the British Association, Toronto meeting, 1906. Quite another aspect of the chemical relationships of nervous action has been advanced by F. H. Scott (*Brain*, 1905, p. 506; *Abstr.*, 1906, ii, 239). He considers that nerves are able to control changes in proteins, because of a proteolytic enzyme produced in nerve-cells.

these substances can be dissolved out of the heart by alcohol, and can then be used to produce inhibition in another heart. The substance or substances cannot be extracted from a normally beating heart; but we have no information as yet in regard to their chemical composition. They appear, however, not to consist of potassium salts, to which Howell¹ attributes such an important rôle in cardiac inhibition.

Cancer.

I shall conclude my report by again referring to the important question which I took up as the concluding section to last year's report. I then expressed the belief that chemistry will assist in the solution of the many problems that surround the pathology of cancer. For instance, the important observation that the gastric hydrochloric acid is scanty or absent in this disease, even when no actual cancer is present in the stomach itself, cannot be meaningless.² Investigations of the various proteins (nucleo-proteins, &c.) obtained from the tumours have not led to much at present,³ but these substances will have to be still further examined.

Perhaps I was a little too positive when I stated that the parasitic theory of cancer was dead; I ought to have said that all the parasites, animal and vegetable, held responsible by different observers for the disease have hitherto turned out disappointments.

It is difficult to transmit the disease to animals, and this limits the field of observation, but there is a transmissible disease of mice which most pathologists agree is a form of cancer, and from the study of which there are great expectations. This disease was first described by Morau⁴ in 1891, and subsequently by Jensen, of Copenhagen, in 1903. It is a disease of the mammary gland; histologically it closely resembles other cancers; it is followed by metastases (secondary tumours in other parts of the body), and it is malignant; that is to say, it kills the mouse. Whether it is absolutely the same disease as human carcinoma is another question, and at a meeting

¹ *Amer. J. Physiol.*, 1906, 15, 280; *Abstr.*, 1906, ii, 179.

² Full papers on this point by B. Moore and his colleagues will be found in *Biochem. J.*, 1906, 1, 274, 297; *Abstr.*, 1906, ii, 565. See also K. Sick (*Arch. klin. Med.*, 1906, 86, 371; *Abstr.*, 1906, ii, 565; Palmer, *Biochem. J.*, 1906, 1, 398; *Abstr.*, 1906, ii, 786).

³ See, for instance, Neuberg, *Zeit. Krebsforsch.*, 2, 171; *Abstr.*, 1906, ii, 875.

⁴ *Compt. rend. Soc. Biol.*, 1891, pp. 289, 721, 801. Morau's work came at a time before cancer research was in vogue; hence the disease is generally known as Jensen's tumour. Jensen showed that in inoculated mice the new formation is a continuation of the growth of the cells introduced by inoculation. The relative importance of the work of Morau and Jensen has been the subject of recent correspondence in the *Lancet* (Nov. and Dec., 1906), and doubt has been expressed whether the two investigators were dealing with the same disease.

of the Pathological Society in London a few weeks ago the experimental and pathological work on mice was spoken of as futile. This, of course, is the view of an extremist, and the correct attitude should be a more hopeful one. Curiously enough, however, in these mice there is no fall in the secretion of hydrochloric acid in the stomach, but the reverse,¹ so it does appear there are grounds for hesitation in accepting the disease as identical with that in the human subject.

A vast amount of work has been performed in relation to the Jensen tumour. It is transmissible by inoculation from mouse to mouse, and already thousands of mice have borne their part in the investigation. I propose, however, only to deal here with the work that has issued from the New York Cancer Laboratory at Buffalo, because there a distinctly chemical bias has pervaded it.² Chemists as well as biologists have now invaded the territory of the pathologists, and Clowes with his colleagues have kept accurate records of the many thousands of mice they have had under observation. They have found that the disease may not only be given to the animals by inoculation or injection of material from other mice, but also that there is further distinct evidence of infectiousness in other ways. For instance, mice transferred to cages which had not been cleaned, but which had held infected animals long previously, developed the disease. Such observations place this form of carcinoma on all fours with other infectious diseases, and lead one naturally to think that the active agent must be a living organism. What the actual agent is, is still unknown, and it is necessary to exercise extreme caution in drawing conclusions on this point. Some of the micro-organisms described by others are merely due to accidental contamination, and other supposed organisms are really artifacts. Calkins and Clowes draw attention to artifacts both in the nuclei and cytoplasm of the cancer cells, even in material fixed by Zenker's method (alcohol and iodine); the curious inclusions which they describe are artificial, but are found usually in the cells which are undergoing degenerative necrosis, and the method, therefore, is in one sense a valuable one in distinguishing the active cells from those undergoing the process of death which is probably associated with a kind of fatty degeneration.

¹ Copeman and Hake, *Lancet*, 1906, ii, 1276; *Abstr.*, 1906, ii, 875.

² The principal papers are as follows: H. R. Gaylord and G. H. A. Clowes, *Med. News*, Jan. 14, 1905; *Surgery, Gynaecology and Obstetrics*, 1906, 2, 633; G. H. A. Clowes, *Johns Hopkins Hospital Bulletin*, 1905, 16, No. 169; G. H. A. Clowes and F. W. Baeslack, *Med. News*, Nov. 16, 1905; *J. Exp. Med.*, 1906, 481; G. H. A. Clowes and W. E. Frisbie, *Amer. J. Physiol.*, 1905, 14, 173; G. N. Calkins and G. H. A. Clowes, *J. Infectious Diseases*, 1905, 2, 555; G. H. A. Clowes, *Brit. Med. J.*, 1906, ii, 1548; H. R. Gaylord, *ibid.*, 1555.

The tumours, in fact, may roughly be divided into two varieties: (1) those which are growing rapidly, characterised by a high percentage of potassium, with little or no calcium, and (2) those which are old, slow-growing, and necrotic, characterised by a high percentage of calcium, with little or no potassium (Clowes and Frisbie).

The second class of tumours may not only be slow growing; they may even diminish in size, and this may culminate in their disappearance, and the animals recover perfectly without any treatment at all. Bashford stated he had only seen one case of recovery in 3,000 mice,¹ but in the experiments of Gaylord and Clowes spontaneous recovery occurred in 23 per cent. of the cases. The retrogression of the growth is attributed to the development of immune forces, as in other infectious maladies, and the observation led the authors to search for cases of spontaneous recovery in human cancer. They found fourteen apparently authentic cases in previous records, but hearsay evidence of this nature is usually regarded with suspicion, not only by lawyers, but by scientific workers too. I doubt if there are many medical men who would not regard the occurrence of cancer in a human being as equivalent to a sentence of death, and there are certainly none who would advise their patients to trust to spontaneous cure instead of submitting themselves to that surgical interference which alone can avert the final disaster.

The high percentage of spontaneous recovery in mice can be still further increased by treatment on the lines of serum therapeutics. The mice which recover possess an active immunity against further inoculation, and if cancer material from the Jensen tumour is mixed with the serum of the recovered mice, and then injected into fresh animals, quite a large percentage of the latter escape the bad effects of the injections. Injection of the serum leads also to more frequent and more rapid recovery.

These and similar statements require confirmation, but such results certainly make one feel there is hope in serum treatment in human carcinoma, and should still further stimulate research in that direction. This hopefulness, however, depends on the assumption that human carcinoma and mouse carcinoma are identical or at least similar diseases. We have already seen grounds for doubting the identity if in one there is a rise and in the other disease a fall in the hydrochloric acid secreted by the stomach, for this is an index of an altered condition in the ions of the blood.

¹ Report of Imperial Cancer Research Fund, 1905. Subsequently he withdrew this statement, as in later work (*Brit. Med. J.*, July, 1906) he found spontaneous recoveries in large numbers, in some series as high as 50 per cent. Immunity developed in mice with the disease was also found by Ehrlich (*Experimentelle Carzinomstudien*, April, 1906).

The relative non-malignancy of the mouse tumour is an additional season for making one hesitate in regarding the two diseases as the same.

Be that as it may, and only the future can decide the question, the results obtained by Clowes and others are important and suggestive; I will only add one more detail of this work, and so bring this report to a close.

Clowes and Baeslack found that the incubation of the mouse-cancer material before it was injected into other animals altered its virulence. Some of their material was, comparatively speaking, inactive; that is to say, a large percentage of the mice injected did not "take." If this inactive material was kept in the incubator for some time previous to injection, its virulence rose, and the percentage of affected mice increased. This, of course, is analogous to what one finds in most other infective substances.

In other cases the material was virulent at the ordinary temperature, but the virulence was lessened after incubation at body temperature; this was the material obtained from necrotic tumours with a high calcium percentage. In order to explain these results it is necessary to assume the existence of a toxin. The toxin acts as a chemical stimulus to cell-proliferation, and its action is accelerated by elevation of temperature; hence, comparatively inactive material is rendered more virulent by the employment of the incubator. But if the toxin is already abundant, it is quite conceivable that the raising of the temperature will lead, not to multiplication, but to destruction of the cells, especially in tumours where necrotic changes have already been initiated by other means. This autolysis will naturally reduce the virulence of the tumour material.

In order to explain the toxin, it is necessary to assume the existence of some agent which will produce it, presumably a living organism, but on that final point we have at present no light.

W. D. HALLIBURTON.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE record for the year 1905 was concerned largely with the "search for nitrogen," or, rather, for means by which that widely distributed, though inert, gas could be made to lend itself to the service of agriculture. This question remains the prominent one to-day, and ever and again hopes have been quickened by some new and startling announcement, and it would seem, indeed, that the day is not far distant when the falling-off of the supplies of nitrate of soda from South America may be contemplated with resignation, and the atmosphere, with its vast store of nitrogen, be laid under contribution to agriculture's needs. The work of the year 1906 has brought this prospect somewhat nearer, although perhaps not very materially so, and development has hardly taken any new form.

Just as the year 1905 closed a new revelation was promised as regards the behaviour of plants in relation to their power of utilising nitrogen, but closer examination has shown the views thus put forward to be untenable. At the close of 1906, there was, similarly, promised a new discovery, whereby atmospheric nitrogen could be cheaply utilised. In each case the details were not at hand at the time of writing, and so it has not been possible to do more than merely chronicle the event. But it is evident that deep interest must attach to researches in this direction, both from the scientific and the practical side of agriculture. The great problem is, of course, how the nitrogen of the atmosphere can be bound up in some form in which it can be transported to the land and there made use of just as nitrate of soda and other nitrogenous materials are. The ways already discovered of effecting the union of nitrogen and oxygen, which have resulted in the production of cyanamide on the one hand and of calcium nitrate on the other, have been further exploited with the view of removing the one great obstacle to the general employment of these materials—namely, their cost of production. It is in this direction that the latest discovery is stated to tend. Meanwhile, information is being

accumulated as to the practical uses and comparative values of these materials so far as their limited supply allows.

In another direction attention is being turned to the work of organisms in the soil, and to the conditions under which some of these, at least, have the power of elaborating nitrogen into forms available for plant use. For the moment, the direct inoculation of leguminous crops, to which so much attention has hitherto been given, seems to have been dropped, and there is little that is new to record about it. But in regard to *Azotobacter* and other soil-organisms, much further work has been done, and our knowledge regarding their action is beginning to shape itself into form. Similarly, inquiry has been pursued as to whether plants do not, in some cases, take up ammonia directly.

In regard to the root action of plants, more evidence has been collected in support of the contention that there is no external action of the root sap itself, but that it is the excretion of carbon dioxide from the roots which assists the solvent action of the soil water. Striking proof has been afforded of the important part which calcium carbonate plays in respect of plant life and crop production, whilst the special place which magnesia occupies has also been investigated.

The inquiry into green-manuring has been continued, and further results have been obtained which bear out the conclusion previously come to that green crops act very variably, and that the deductions formed from theoretical considerations are not borne out in farm practice.

Much work has also been done with regard to the question of "strength" in wheat and what is implied by this, but strong indications are given that the solution of the problem will not come from the chemical but from the biological side. Different branches of the work of the Rothamsted Experimental Station have been summarised in various useful ways, among which may be mentioned a survey, by N. H. J. Miller,¹ of the amount and composition of the drainage water through unmanured land, as recorded at Rothamsted from 1870 until the present time.

A distinguishing feature of the year has been the revival of interest in the sugar industry, and reference is made to several papers dealing with questions affecting this industry.

In India the advance indicated in last year's report has been very marked indeed, a thorough scheme of agricultural investigation having been now set on foot. An Imperial Department of Agriculture² has been formed, comprising eleven different appoint-

¹ *J. Agric. Sci.*, March 1, 1906, 377.

² *Annual Report of Imp. Dept. of Agriculture*, 1904-5, Calcutta, 1906.

ments, included in which are those of an inspector-general, a director, an agricultural chemist, two botanists, an entomologist, and a bacteriologist. Provincial Departments have also been established in Bengal, the Punjab, and the Central Provinces, whilst the existing Departments in Madras, Bombay, and the United Provinces have been strengthened. In the Bombay and Central Provinces there is also an agricultural chemist attached in each case to the Department.

Altogether, the staff of Government experts, which four years ago numbered six throughout India, has now been increased to twenty-five. A research institute has been opened at Pusa, in Behar, and includes fully-equipped laboratories for research work, an experimental farm, a cattle-breeding farm, and a higher agricultural college.

The Indian Tea Association has continued its investigations with more assiduity than ever, and, under its able expert, Dr. H. H. Mann, has put forward some really excellent work, more especially on the subject of the fermentation of tea. The account of Dr. Mann's investigations shows most clearly how well-directed science may be utilised for the benefit of an industry. Under the direction of the Imperial Department, scientific aid has also been given to the, unfortunately decaying, indigo industry.

The obituary for the year includes the names of Prof. Alexander Müller, of Sweden and Berlin, and of Prof. Adolph Emmerling, of Kiel. The former was the organiser of the first agrico-chemical "Versuchs-Station" in Stockholm, and was specially known for his work on moor soils, on the nature of milk constituents and the influence of foods on the composition of milk, as well as, later in Berlin, for his researches on the utilisation of sewage and the purification of streams. Emmerling was best known for his researches on the formation of albumen in plants.

Among publications may be noted a new edition (8th) of "Church's Laboratory Guide," which has been thoroughly revised and practically rewritten by Prof. Edward Kinch, of Cirencester, also the "Microscopy of Vegetable Foods," by A. L. Winton (Connecticut, U.S.A.), which is practically an American edition of Dr. Josef Moeller's well-known work, "Mikroskopie der Nahrungsmittel."

Nitrogen.

(a) Calcium Nitrate.

It is to the direct combination, through electrical force, of the nitrogen and oxygen of the air that attention has been mainly turned, the process briefly described in last year's report, and

resulting in the production of calcium nitrate, being the one that seems to offer the greatest prospects of ultimate success. The product, so far as obtainable, has been tried practically, and with satisfactory results. The entire matter of the development of the process into a regular industry turns purely upon the question of cost. Though calcium nitrate has been made, and used, it cannot yet be said to be a regular article on the market; there is no price quoted for it, nor is it open to anyone to purchase a supply of it, or to use it just as he would any other artificial fertiliser for his soil. Even where it has been tried experimentally, it has been procured with difficulty, and, up to the present, it cannot be said that there is more than a pure "estimate" of the cost of its production. In such circumstances the whole question of the material becoming a regular article of commerce, and competing successfully with nitrate of soda, depends entirely on its production at a cost which will enable the nitrogen in it to be supplied at a lower rate than the same amount of nitrogen in the form of nitrate of soda. Though the works of Birkeland and Eyde, at Nottoden (Norway), continue to turn out a certain quantity of calcium nitrate, it does not seem that the process can, as yet, be profitably worked; otherwise, calcium nitrate made by this process would, by now, be a regular article on the market. Other works have been established at Ludwigshafen, and also in Italy. At a quite recent date, however, has come the announcement of a new "discovery," with which the names of Crookes and of J. von Krowalski and I. Moscicki, of Freiburg, Switzerland, are associated. The details are still wanting, but we are led to suppose that the new method really consists in some improvement, possibly in technique, on the Birkeland and Eyde system, whereby greater efficiency is attained, and the calcium nitrate produced at a lower cost than before. It has, at the same time, been stated that the methods are entirely different from those in use in Norway, that there is a higher percentage of "output" than by any other system, and that "pure concentrated nitric acid" is produced. Naturally one must await, and with interest, the further details of this discovery, but, whatever be the outcome, it would seem to be fairly established that the process can only be worked at places where enormous water power is available, and hence there is no likelihood of England becoming a producing country.

From the few recorded experiments which have, so far, been made with calcium nitrate, the following may be noted.

J. Sebelien,¹ using the basic calcium nitrate suggested by R. Messel, found the results, as between this and sodium nitrate

¹ *J. Landw.*, 1906, 54, 159.

yielding the same amount of nitrogen, to be somewhat variable. Where better results were obtained with calcium nitrate this was not infrequently proved to be due to the lime in the calcium nitrate, for, when lime was added to sodium nitrate equally good results were given. On a peaty soil calcium nitrate did as well with cereals as did sodium nitrate, and this was also the case with grass land. The latter experiments were carried out in Norway. These results are only what one would expect, and, as has been pointed out, there is no reason why calcium nitrate should not do as well as sodium nitrate, whilst, where lime is deficient in a soil, it might be expected to be superior, because of the lime it supplies to the land.

(b) *Cyanamide.*

The production of calcium cyanamide has continued, and, to judge from the experiments made with it, it would seem to be more generally obtainable than calcium nitrate, though it, too, cannot yet be reckoned as a staple commercial product, or to have a regular market price quoted for it. Experiments made with it on crops have given variable results, some observers holding that it gives equally good results as ammonium salts, others distinctly limiting its practical application to particular kinds of soil and to particular conditions. Its use on soils containing much vegetable matter (humus) is generally agreed upon as not being attended with benefit.

F. Löhnis¹ states that the nitrogen of calcium cyanamide is rapidly transformed into ammonia in April and May, and that its action on crops is very like that of ammonium salts. C. von Seelhorst and A. Muther,² in carrying out pot-culture experiments with it, found that on sandy loams and loams it did quite as well as ammonium sulphate, but that in sand cultures it was injurious to vegetation. They attributed this to the presence of some calcium carbide, and showed that if iron oxide was added to the sand the injurious action was prevented. H. von Feilitzen³ came to the same conclusion as regards cereals on sandy soils and loams, but states that on peaty soils calcium cyanamide has very little effect with oats or potatoes. J. Sebelien⁴ likewise found that calcium cyanamide had little effect, or was even injurious, in the case of cereals grown on peaty soils; and with grass land, in Norway, he obtained results inferior to those attending the use of sodium or calcium nitrate. A. Stutzer⁵ has carried out pot experiments on rye with calcium cyanamide as compared with

¹ *Centr. Bakt. Par.*, 1905, [ii], 15, 430.

² *Chem. Centr.*, 1906, i, 584.

³ *Landw. Versuchs-Stat.*, 1906, 65, 275.

⁴ *J. Landw.*, 1905, 53, 329.

⁵ *J. Landw.*, 1906, 54, 159.

ammonium sulphate and sodium nitrate, and states that 68.4 per cent. of the nitrogen was recovered in the crop with ammonium sulphate, 65.9 per cent. with cyanamide, and 55.2 per cent. with sodium nitrate. In the last-named case the nitrate was, however, applied in the autumn, and may thus have suffered loss by drainage in winter. Paul Wagner¹ also finds that in "normal soils" cyanamide works quite well, but that on acid soils and on sandy ones rich in humus and poor in lime its action is uncertain. He further maintains that it can quite well be used as a top-dressing, if applied about February, to winter crops. He admits that if applied in warm weather there may be loss of ammonia. Löhnis has already pointed out objections to the use of cyanamide: that it cannot be used as a top-dressing, nor be mixed with superphosphate, owing to the mixture getting hot; that it deteriorates in damp weather; and that, when applied to the soil, ammonia is evolved, which is injurious at first to the germination of the seed.

E. Wein² says, as the result of field experiments, that cyanamide is as good as ammonium sulphate, and he finds it to be as effective as sodium nitrate on peaty soils, provided that they contain plenty of calcium carbonate. In Japan experiments have also been tried by K. Asō³ on buckwheat, *sesamum*, hemp, and rice, with results generally equal to those from ammonium sulphate and nitrate of soda, provided that the soil be not rich in humus.

F. Löhnis⁴ has investigated the changes which calcium cyanamide undergoes in ordinary soils. He states that it is decomposed by certain bacteria, ammonia and, possibly, nitrates being formed. Among the bacteria capable of producing the decomposition are *Bacterium Kirchneri* and *B. lipsiense*. Pure cultures of each of these, however, do not severally act as effectively as do mixed cultures of the two. The decomposition does not take place in boggy soils, either because the bacteria may not be there, or because the cyanamide is converted by the organic acids present into compounds that are hurtful to vegetation. The decomposition is not facilitated either by the free admission or the exclusion of air, so that stirring the soils has no effect in hastening the change.

From these various experiments it may be regarded as fairly established that under favourable conditions and with suitable soils (such, mainly, as are not rich in humus or deficient in lime) calcium cyanamide is practically nearly as good, nitrogen for nitrogen, as

¹ *Deutsche Landw. Presse*, Aug. 18, 1906.

² *Chem. Centr.*, 1906, ii, 1454.

³ *Bull. Coll. Agr. Tōkyō*, 1906, 7, 47.

⁴ *Bied. Centr.*, 1906, 35, 375.

ammonium sulphate or sodium nitrate; but that it is non-effective in the case of peaty soils or those with little lime in them; also that it does not lend itself to ready use as a top-dressing, for storage, or for mixing with other materials. To come back to the main question, that of cost, it is clear that the extended use of cyanamide must depend on whether the nitrogen in it can be supplied at a less cost than the same amount of nitrogen in the form of sodium nitrate or ammonium sulphate; and on this point there is, as yet, no definite information. It may be added that the information as to the cost of producing calcium nitrate is even less certain. It is also well to point out that, with few exceptions, the experiments so far recorded with cyanamide have been pot experiments, and, however useful these may be as an indication, they need the confirmation of field experiments before they will command the attention of the practical agriculturist.

Suggestions have been made as to combining cyanamide with other materials. Thus, F. T. Shutt and H. W. Charlton¹ have formed calcium cyanamidocarbonate by passing carbon dioxide gas through a solution of calcium cyanamide. This product, if kept low in amount, will not injure the germination of seeds, but if the quantity be increased above 5 milligrams per 100 grams of soil, germination is affected, and with increasing quantities is quite destroyed. Nitrification in the soil is also decreased, showing that the nitrifying organisms in it are affected. Suggestions have also been made to add to the calcium carbide, before heating, one or more fluorides of an alkali or alkaline earth.² By this means, it is said, calcium cyanamide is obtained at a lower temperature.

(c) *Leguminous Nodules.*

It has been mentioned that work in the direction of the inoculation of leguminous crops with the corresponding nodules has been, for the time, nearly put aside. The experiments instituted in Great Britain by the Board of Agriculture in 1905, and which were carried on in 1905, both with the German (Hiltner) preparation and the American (Moore), were the reverse of encouraging, and in the few cases in which these experiments were carried on for a second year (1906) with a cereal crop following the leguminous ones anything of much note has been obtained. From the Continent and, America one hears also of but little more done in this direction, but at all events, the day has not come yet when the farmer will order leg-kets of "inoculating material" for his bean, clover, and other leguminous crops. At the Woburn Experimental Farm the

² O *Trans. Roy. Soc. Canada*, 1905, [ii], 11, (8), 73.

F. Carlson, Stockholm, Eng. Pat. 15,445, July 7, 1906.

experiments were continued in 1906, a wheat crop being taken after the leguminous ones. The only further point brought out was that, whether sterilised soil, poor soil, or rich soil was used, the wheat crop was in each instance decidedly poorer after tares taken previously than after peas or beans.

H. Flamand¹ has investigated, by water-culture experiments, the influence of different salts on the process of symbiosis, as measured by nodule development. Peas, beans, and tares were the crops tried, and the plants were inoculated from appropriate nodules. Potassium nitrate (1 : 10,000) altogether prevented nodule formation, but sodium nitrate only did this when the quantity was increased to 1 : 2000. Potassium phosphate was beneficial to nodule formation in the cases of peas and tares, potassium chloride and potassium sulphate being less so, although for beans potassium sulphate was best. Calcium and magnesium salts generally were beneficial to peas and beans, but only calcium sulphate for tares. It must be said, however, that there is a good deal that seems contradictory in these experiments, and doubt must be cast upon the variable results obtained with plants so very much alike as peas and beans.

(d) *Direct Utilisation of Nitrogen by Plants.*

As briefly announced in last year's report, a revolution in our ideas as to the capability of plants generally to take up nitrogen from the air was promised by the statement of T. Jamieson, of Aberdeen,² to the effect that he had discovered that not only leguminous plants, but cereals, grasses, &c., had the power, exercised through certain structures on their leaves and leaf-stalks, of taking in directly the nitrogen of the atmosphere. Jamieson rejected the nitrogen theory of Lawes and Gilbert, and the "nodule" theory of Hellriegel, and maintained that because he found on plants in their early stages certain organs the cells of which contained albuminous matter, the nitrogen of this was derived direct from the air, without any process of symbiosis. Naturally such a view was stoutly assailed by vegetable physiologists and agricultural chemists. Its untenability was shown by Bayley Balfour, of Edinburgh, who pointed out that the above afforded no proof whatever of fixation of nitrogen, and that on this theory it might as well be assumed that every living cell of a plant, including those of the root, possessed this same property; the presence of albuminous matter in a cell was no evidence of direct assimilation of nitrogen from

¹ *Bied. Centr.*, 1905, **34**, 738.

² *Agricultural Research Association, Aberdeen, Report for 1905.*

outside. Agricultural chemists also pointed out that the theory could not be accepted unless direct experimental and quantitative proof were afforded of the plant being placed in an atmosphere containing a known amount of nitrogen and of its removing from this a quantitative amount of nitrogen. Accordingly, we have to go back upon our former ideas, and the problem of nitrogen supply still remains with us.

(e) *Nitrogen Assimilation by Soil Bacteria.*

To this subject, and more especially to the work of the organism *Azotobacter chroococcum*, much attention has been given.

R. Thiele,¹ while allowing that *Azotobacter* can fix nitrogen, expresses doubt as to whether this is an inherent property, and whether it may not frequently, even in normal circumstances, be lost. He has worked out the conditions of temperature most favourable for fixation to proceed, and points out that fixation is less according as the most favourable temperature is only occasionally attained.

J. Stoklasa² finds that *Azotobacter chroococcum* possesses more power than any other species for fixing atmospheric nitrogen. Both dextrose and mannitol will serve well as culture media. The former is the better, but the addition of a little calcium carbonate is necessary with it. Stoklasa has estimated quantitatively the amount of carbon dioxide evolved during the assimilation process; on an average 1 gram of *Azotobacter* dry substance will evolve 1.27 grams of carbon dioxide in 24 hours. Under similar conditions *B. Hartlebi* will evolve 0.6 gram, and *Clostridium gelatinosum* 0.48 gram, so that *Azotobacter* is much the most active. When dextrose is used as the culture medium, lactic, acetic, and formic acids are the decomposition products, together with carbon dioxide and hydrogen. Stoklasa considers the assimilation process to be related to the respiratory process. He differs from Beyerinck's view that *Radiobacter* has an appreciable power of assimilating atmospheric nitrogen, but considers it a denitrating organism; a mixed culture of *Azotobacter* and *Radiobacter* has less power of assimilating nitrogen than a pure culture of *Azotobacter*, and *Radiobacter* will reduce the greater part of the nitric acid to free nitrogen, whilst a certain proportion is fixed in the form of organic bodies, chiefly nucleo-proteins. S. F. Ashby³ has also worked on the assimilation of free nitrogen by *Azotobacter chroococcum*. In making cultures of soil organisms,

¹ *Ländw. Versuchs-Stat.*, 1905, **63**, 161.

² *Zeit. angew. Chem.*, 1906, **19**, 803.

³ *J. Agric. Sci.*, **2**, Jan. 1907, ³35.

using mannite as a medium, he found that the greater the aëration was (namely, when less mannite was used) the greater was the amount of nitrogen fixed per gram of mannite oxidised. Further, when *Azotobacter* was present the average yield of nitrogen was doubled. Still, fixation took place, although low in amount, even when *Azotobacter* was absent. The average fixation was 6.95 milligrams of nitrogen for 1 gram of mannite when *Azotobacter* was present, and 3.22 milligrams when it was absent. Aëration and the presence of a base would appear to give favourable conditions to fixation. Ashby compared the influence of magnesium carbonate and calcium carbonate as bases in relation to fixation. He found that magnesium carbonate delayed development at first, but that ultimately the yield of nitrogen was larger than with calcium carbonate. By taking soil at different depths Ashby showed that *Azotobacter* was present in greatest abundance in the soil near the surface. He noticed, too, that the organism would stand drying up quite well, and would produce abundant growth if fresh culture solution were poured over the mass. Hence it is clear that the organism can be carried about as dust by wind. B. Heinze¹ attributes the importance of algæ in fixing nitrogen in soils to their supplying nitrogen-fixing organisms, and chiefly *Azotobacter*, together with carbonaceous food. It is not the case, as has been stated, that all that algæ do is to prevent loss of ammonia in the soil.

E. Haselhoff and G. Bredemann² ascertained that anaërobic nitrogen-assimilating bacteria (*Clostridia*) are abundantly present in soils and in the leaves of forest trees; the amount of assimilation is about equal to that of *Clostridium Pasteurianum*, namely, 2.74 milligrams per gram of dextrose or mannite.

Nitrification.

S. F. Ashby³ has studied the question as to whether anything will replace carbonate of lime as a base for nitrification. Kaolin and modelling clay were tried, but neither was found effective; ferric hydroxide, however, will act, but is inferior to calcium carbonate. Ashby comes to the conclusion that a neutral ammonium salt is not directly nitrifiable, but that the function of a base is to form ammonium carbonate, which is nitrifiable. Of bases, the reaction with magnesium carbonate is greater than with calcium carbonate. This latter observation is confirmed by

¹ *Centr. Bakt. Par.*, 1906, **16**, [ii], 640.

² *Landw. Jahrb.*, 1906, **35**, 381.

³ *J. Agric. Sci.*, **2**, Jan. 1907, 52.

S. Machida,¹ who found nitrification to be favoured by magnesium carbonate more than by calcium carbonate.

A. Müntz and E. Lainé² carried out experiments with the object of producing nitrates in large quantity. Animal charcoal was found to be an excellent medium for nitrifying organisms, and with a solution of 0.75 per cent. of ammonium sulphate ten square decimetres produced 8.1 grams of sodium nitrate per day. If stronger solutions were used, nitrification was less active. They also tried experiments with soil to which 0.2 per cent. of ammonium sulphate was added, and it produced nitrates at the rate of 350 grams per cubic metre per day, which, taken to a soil depth of half a metre, was equivalent to 1,750 kilos of sodium nitrate per hectare. The same authors, in another communication,³ show that humus, in whatever amount, is not prejudicial to nitrification, but indeed is rather favourable to it. It is not, however, necessary, as nitrification can be obtained in soils poor in organic matter. Humus seems to aid the multiplication of nitrifying organisms, and, as a rule, a soil contains more active organisms and is more prone to enter into nitrification according as it contains more humus. Different soils showed very different effects as regards nitrification, and rich soils nitrified much more quickly than sandy or clay soils. With the same amount of ammonium sulphate a rich soil, with 17.6 per cent. of carbon, nitrified, at the end of seven days, 0.209 grams of nitrogen per kilogram as against 0.02 gram with a soil containing only 1.5 per cent. of carbon. Peat was found to be the best medium for nitrifying organisms, and by passing a 0.75 per cent. solution of ammonium sulphate over a peat bed charged with nitrifying organisms nitrates were formed at a rate much in excess of anything previously obtained. The most suitable temperature is 30°.

The process of nitrification with regard to the purification of sewage has been studied by Harriette Chick.⁴ The investigations were made during the filtration of sewage. The evidence goes to show that nitrification takes place in two stages, and is due to the action of two classes of organisms, the first producing nitrites and the second converting these into nitrates. The organisms would seem to be the same as those which produce nitrification in the case of soils. It may be considered strange that organisms which are so influenced by the presence of organic matter should be able to carry on their activity; but it is pointed out that they may be in a measure protected by other organisms with which they are

¹ *Bull. Imp. Centr. Agric. Exp. Stn. Japan*, 1905, **1**, 1.

² *Compt. rend.*, 1905, **141**, 861.

³ *Ibid.*, 1906, **142**, 480, 1239.

⁴ *Proc. Roy. Soc.*, 1906, **77**, B, 241.

in symbiosis, or that, while the organic matter collects mainly at the surface of the filter, the nitrifying organisms multiply rapidly in the lower part of the filter, where the organic matter is less in amount. It has also been shown by others that if nitrifying organisms exist in sufficient quantity, they are able to withstand the influence of organic matter that might otherwise destroy them. Whether the two stages of nitrification go on together or at separate intervals depends on the condition of the sewage, whether very ammoniacal or not. If strongly ammoniacal the change into nitrates may be delayed until more of the ammonia has been converted into nitrites. There would appear to be no evidence whatever as to the retention of free and active ammonia in coke filters without nitrification, but that nitrification takes place rapidly. The opinion is expressed that continuous filtration is a better system than that of contact beds, aëration being more complete in the former, diffusion more efficient, the distribution of the different stages of purification better, and the facilities for cleaning greater.

J. E. Purvis and C. J. Coleman¹ have studied the influence of the saline constituents of sea water on the decomposition of sewage. They used not only sea water itself, but solutions containing the various salts separately, and mixed in the proportions in which they occur in sea water. The general conclusion was that both sodium chloride and sea water hindered very greatly the production of nitrates. Instead of the decomposition of the sewage into carbon dioxide, water, and nitrates taking place, highly complex nitrogenous compounds seemed to remain in solution, and oxidation to proceed very slowly. The authors draw the practical conclusion that it is a mistake to run sewage straight into the sea without previously treating it by some filtration or bacterial process.

E. J. Russell and Norman Smith² examined the question as to how far purely physical and chemical processes which take place in the soil may contribute to the formation of nitrites and nitrates, independently of the action of bacterial processes. The first point to meet was the contention of Schönbein that ammonium nitrite was formed during the distillation of water in air or during its rapid evaporation. The authors repeated the experiments, and critically discuss the work of Schönbein and his successors, and they find no evidence whatever of the production of nitrites during the evaporation of water from the soil under any of the varied conditions which obtain in it. Further, they find no evidence of the capability of the soil to effect the combination of nitrogen and oxygen. Oxidation of free nitrogen may, they think, possibly take

¹ *J. Sanit. Inst.*, 1906, **27**, 8, 433.

² *J. Agric. Sci.*, **1**, March 1906, 444.

place by induced oxidation processes, but the evidence accumulated would lead to the conclusion that this is at best an unimportant source of the production of nitrates under natural conditions.

The development and distribution of nitrates in field soils has been observed by F. H. King, J. A. Jeffrey, and A. R. Whitson.¹ In the surface soil, to a depth of 1 foot, nitrates increased from April to June, and then there was a decrease, due probably to rapid growth or heavy rains. Nitrates were much less abundant in the second foot of soil than in the first, and in a dry season there was a tendency for nitrates to accumulate near the surface. Further determinations made between November and April showed that there were no more nitrates in the soil after the winter frosts than before these set in.

Denitrification.

R. Hornberger,² by exposing leaves of oak, beech, &c., for a year to air and rain, found that in the majority of cases there was a greater loss of nitrogen than gain of it.

The influence of carbohydrates and organic acids on the denitrification process has been investigated by J. Stoklasa and E. Vitek.³ The micro-organisms studied were grown in a solution containing sodium nitrate, potassium, calcium and other salts, along with the particular carbohydrate or organic acid. *Clostridium gelatinosum* produced, in the case of dextrose, ammonia most freely. *Bacillus subtilis* gave ammonia best when lævulose or galactose was the carbohydrate. *Bacterium Hartlebi* in arabinose solutions formed much organic nitrogen, and arabinose generally proved a better medium than xylose. Organic acids, again, were excellent media for the decomposition of nitrates to elementary nitrogen, and for the formation of organic nitrogen compounds. Further investigation as to the stages in which the action proceeded showed that the denitrification process took place in two steps, the first being the reduction of nitrate to nitrite by means of the hydrogen formed along with carbon dioxide by the decomposition of the carbohydrate or organic acid through the enzyme of the micro-organisms. From this it is argued that the carbohydrates in a soil are more likely to serve for the purpose of converting nitric acid into ammonia than as nutrients for denitrification bacteria.

J. Stoklasa, J. Jelínek, and A. Ernest⁴ further show, from experiments with sugar-beet soils, that the organic matter in the soil

¹ *Agr. Exper. Stat. Univ. Wisconsin, 20th Annual Report*, 339.

² *Bied. Centr.*, 1905, **34**, 726.

³ *Zeit. Zuckerind. Böhm.*, 1906, **31**, 67.

⁴ *Ibid.*, **30**, 223.

is not a suitable source of carbon for denitrifying organisms, and that nitrates are not, to any material extent, reduced to nitrogen. When soils are well cultivated, and hence well aerated, loss of nitrogen will not occur, though nitrates may be reduced to nitrites.

Decomposition of Nitrogenous Matter in Soil.

F. Löhnis¹ found that *Bacillus mycoides* and *Bacterium vulgare* respectively converted within three weeks 39 and 28 per cent. of the total nitrogen of bone-meal into ammonia; George S. Fraps,² similarly, found the organisms producing ammonia from nitrogenous fertilisers to be most active during the first week; after the third week their influence decreased and nitrification was more marked.

Nitrogen in Rain.

J. W. Leather³ has determined the amount of nitrogen present as ammonia and nitrates in a year's rainfall at Dehra Dun and Cawnpore (India). He obtains the following figures for a complete year:—

		Parts per million.		Pounds per acre.		Total.
Rainfall, inches.		As ammonia.	As nitrate and nitrite.	As ammonia.	As nitrate and nitrite.	
Dehra Dun	86.48	0.104	0.070	2.037	1.368	3.405
Cawnpore .	49.36	0.221	0.068	2.482	0.768	3.250

These figures do not differ widely from those found at Rothamsted, where the total nitrogen is 3.840 lb. per acre, made up of 2.712 lb. as ammonia and 1.128 lb. as nitrates and nitrites, so that no countenance is given to a general belief that the Indian rainfall is richer in nitrogen than that of England. At Dehra Dun, however, where thunderstorms are more frequent than at Cawnpore, it is noticeable that there is considerably more nitrogen present as nitrates. At Cawnpore the dew was also collected and analysed, but difficulties connected with the collection are great. The results, so far as obtainable, show a total of only 0.111 lb. of nitrogen per acre during the year, this being equally divided between that existing as ammonia and that as nitrates. The total dew was 0.170 inch, and therefore, as a supply of combined nitrogen, cannot be considered of importance.

H. Ingle⁴ has done the same in regard to the rainfall collected

¹ *Centr. Bakt. Par.*, 1905, [ii], 15, 430.

² *J. Amer. Chem. Soc.*, 1906, 28, 213.

³ *Imp. Dept. Agric. Annual Report*, 1904-5 (Calcutta, 1906), 55.

⁴ *Transvaal Agric. J.*, 1905, 4, 104.

at Pretoria (South Africa.) The rainfall of 24·31 inches per annum supplies 7·670 lb. of total nitrogen per acre, 6·587 of which occur as ammonia and 1·083 as nitrates. The total nitrogen, it will be noted, is about double that of Rothamsted, and the proportion present as ammonia relatively higher.

N. H. J. Miller¹ in stating the results of the Rothamsted rainfall in regard to nitrogen and chlorine contained, gives a summary of results from 30 different places in tropical and non-tropical countries, and points out that great differences in climate do not coincide with material differences in the amounts of nitrogen brought down by the rain, but that, whilst in non-tropical countries most of the nitrogen is present as ammonia, in tropical countries the proportion of nitric nitrogen is relatively higher.

The subject of rainfall in connexion with drainage through uncropped land has led E. J. Russell² to examine more closely the Rothamsted results obtained respectively with the 20 inch, 40 inch and 60 inch drain gauges there. He observes that the relation between the evaporation from the three gauges is not constant; at first evaporation from the 20 in. gauge is lowest, then it increases, exceeds that of the 40 in. gauge, and, after twenty years, that of the 60 in. gauge as well. He attributes the variations to a "secular change" in the drain gauges, and suggests that this is due to a decrease in the amount of organic matter in the soil of the gauges, and to the action of rain in washing out the finest particles, this resulting in an increased evaporation of water.

Green-Manuring.

Allied to the "nitrogen question" is that of the supply, through green-cropping, of nitrogen to soils. The experiments on this subject, recorded for 1903 and 1904 in last year's report, have been continued at the Woburn Experimental Farm,³ and the results for the wheat crop of 1906 succeeding green-manuring in 1905, are now available. Once more it appears that, contrary to theory, the ploughing-in of a non-leguminous crop (mustard) has given a better return in a subsequent corn crop than has that of a leguminous crop (tares). The green crops were cut and weighed previously to being turned in, the tares giving 7 tons 2 cwt. green produce per acre, containing 1·05 per cent. of nitrogen, and the mustard 5 tons 10 cwt. per acre, with 0·46 per cent. only of nitrogen, the organic matter being nearly alike in amount in the two. When, however, the subsequent wheat crop came to be weighed, the results were:

¹ *J. Agric. Sci.*, 1, Mar. 1906, 377.

² *Ibid.*, 2, Jan. 1907, 29.

³ *J. Roy. Agric. Soc.*, 1906, 67, 299.

	Produce of wheat per acre, 1906.	
	Corn. Bushels.	Straw. Cwt. qr. lb.
After tares ploughed in	24·5	17 1 24
After mustard ploughed in.....	37·6	28 0 15

Thus the leguminous crop (tares) has once again failed to produce the larger crop which one would expect to accrue from the larger supply of nitrogen.

Humus.

S. Suzuki¹ has observed the conditions under which humus formation goes on in soils. Dry powdered oak leaves were moistened and mixed with some humous soil; magnesium carbonate, calcium carbonate, potassium phosphate, and other substances were then severally added in different flasks, and their action studied while humification of the leaves proceeded. The author found that humification proceeded parallel with the formation of carbon dioxide; that magnesium carbonate promoted the development, and that calcium carbonate retarded it, whilst potassium phosphate had a favourable effect.

A. D. Hall, N. H. J. Miller, and N. Marmu² have devised an improvement in the estimation of carbon in soils and similar substances. Recognising that the chromic acid method of Wolff gives too low results owing to incompleteness of oxidation, they have proposed to add a short tube containing red-hot copper oxide to complete the combustion. They find that by this means they can convert all the carbon into carbon dioxide, and the results agree closely with those of combustion in oxygen. The convenience of the method is that, by adopting Brown and Escombe's modification,³ they can first determine the carbon dioxide present as carbonate in a soil, and then, by attaching the copper oxide tube, they can, on the same sample and in the same apparatus, estimate the organic carbon.

Lime and Magnesia in Soils.

Continued interest has been shown in the important part played by lime in soils, and also in the significance of magnesia, and its relation to the lime present. The Woburn Field Experiments⁴ afford the most striking example of the absolute need of lime in a soil, more especially under the influence of the continuous application of ammonium salts, these latter bringing about, in

¹ *Bull. Coll. Agric. Tōkyō*, 1906, 7, 95.

² *Trans.*, 1906, 89, 595.

³ *Phil. Trans.*, 1900, 193 B, 289.

⁴ *J. Roy. Agric. Soc.*, 1906, 67, 284, 285.

the best results by making the ratio of CaO to MgO 1 : 1. On the other hand, S. Maki and S. Tanaka¹ showed that if land be over-limed, it may be benefited by adding magnesium sulphate to it. Manuring with magnesium sulphate has been tried in several instances (magnesium carbonate being difficult to obtain in Japan), and it is found that it has about seven times the efficacy of magnesite, so that when magnesium sulphate is used the ratio of CaO to MgO should be 7 : 1, whereas with magnesite it should be 1 : 1.

Interesting as these results in regard to lime and magnesia are, it has to be remembered that the experiments have been with pot-culture only, and they need the confirmation of field work. It would be very desirable to gather experience from field soils containing lime and magnesia in different relative proportions, and to ascertain if the general results obtained in pot experiments hold good in actual practice.

Phosphates.

D. N. Prianischnikoff² has experimented on the relative value of different phosphates. In sand culture the effect of bone meal was about 50 to 60 per cent. of that of soluble phosphates, and when a crude phosphate, like phosphorite or apatite, was used, although gramineous crops improved very little, lupins did so considerably. In sand cultures ammonia salts had the power of rendering even very sparingly soluble phosphates available for the use of plants. The same author,³ working with aluminium phosphate and iron phosphate, found that millet, vetches, and mustard, grown in sand, would assimilate the phosphoric acid from aluminium phosphate, either when merely dried or when ignited, as also from iron phosphate if merely dried, but not if ignited. Rye and wheat, however, could not utilise the phosphoric acid of crude phosphates, although lupins did as well with crude phosphate as with bone phosphate.

Different processes have been suggested for rendering raw phosphates available for use. One of these is that of the Wolters Phosphat. Gesellschaft,⁴ in which raw phosphates are melted in a Siemens' furnace with alkali silicates and lime, the product being then led into cold water, when nearly all the phosphoric acid is found to be soluble in citrate solution. The materials suggested for use are:—Tricalcium phosphate 40 per cent., silica 30 per cent., lime 14 per cent., soda 16 per cent.

¹ *Bull. Coll. Agr. Tōkyō*, 1906, **7**, 61.

² *Landw. Versuchs-Stat.*, 1906, **65**, 23.

³ *Bied. Centr.*, 1905, **34**, 741.

⁴ Eng. Pat. 9183, April 18, 1906.

The influence of phosphoric acid on straw has been observed by D. Lienau and A. Stutzer,¹ who conclude that it promotes the thickening of the cell wall. This effect is, however, greatly diminished if much potassium, calcium, or nitrogen is present. The smaller the amount of total ash and of potassium in the straw, the greater will be the thickening of the cell walls; the application of phosphates has the effect of reducing these quantities, whilst the amount of phosphoric acid in the straw is found not to be itself dependent on the quantity supplied as manure.

G. André² determined at various stages the phosphoric acid and nitrogen in the sap of certain quickly-growing annuals (*Papaver* and *Pyrethrum*), with the result that the nitrogen in the sap was shown in general to diminish as the phosphoric acid increased. He also found that in annuals a portion of the phosphoric acid migrated, as soluble mineral phosphate, from the leaf to the ovule, while another portion is removed in combination with nitrogenous organic substances.

W. Windisch and W. Vogelsang³ have investigated the nature of the phosphoric acid that occurs in barley grain. In making a cold-water infusion of barley they found that this contained phosphoric acid of which a considerable portion was in the inorganic state. But when the infusion was made in such a way as to exclude the action of enzymes, the whole of the phosphoric acid was found to be in the organic state, and they conclude that raw barley contains no inorganic phosphates, but that these are only produced when the organic compounds are, as in the steeping and malting processes, subjected to the hydrolytic action of the enzymes. This change goes on better in the dark.

W. Zaleski,⁴ from experiments with seedlings of *Lupinus angustifolius*, has come to the same conclusion regarding the action of enzymes on proteins containing phosphorus, and shows that inorganic phosphates are in this way produced.

A. D. Emmett and H. S. Grindley⁵ have similarly examined the phosphorus-containing substances in flesh, and find that in beef 75 per cent. of the total phosphorus is soluble in cold water, and that one-fourth of this consists of organic compounds.

¹ *Landw. Versuchs.-Stat.*, 1906, **65**, 253.

² *Compt. rend.*, 1906, **142**, 106, 249.

³ *Woch. Brau.*, 1906, **23**, 516.

⁴ *Chem. Centr.*, 1906, ii, 893.

⁵ *J. Amer. Chem. Soc.*, 1906, **28**, 25.

Availability of Phosphoric Acid in Soils.

A. D. Hall and A. Amos¹ have further investigated the means of determining the amount of plant food—especially phosphoric acid—which may be reckoned as being immediately “available” for plant food. They criticise B. Dyer’s citric acid method, and point out that, although very useful, it must be regarded as purely empirical, inasmuch as it is based on the now generally abandoned theory of the excretion by roots of acids other than carbon dioxide. The American method of using a $N/200$ solution of hydrochloric acid is similarly criticised. Both leave out of account the nature of what is left in the soil, and presume that this will not in turn become “available” until the soil has undergone a further weathering process. Many circumstances, such as cultivation, the supply of water, the nature of the crop grown, &c., will cause variations in the amounts of the constituents assimilated by the crop. This has led Whitney to regard the soil water as the important matter of consideration, and as possessing a constant composition for all soils, being always in equilibrium. Hall and Amos accordingly adopted the plan of attacking the soil continuously with the solvent, removing the first portion of the solution after equilibrium had been attained. The remainder of the soil was then attacked with a fresh portion of the solvent, and so on. At first the solvent employed was carbon dioxide and water, but, because of the difficulty of filtration, and that some of the soil got into the extract, this was given up in favour of a 1 per cent. solution of citric acid. A period of twenty hours, with constant agitation, was found to suffice for the first separation, and to remove as much phosphoric acid as was extracted when the process was continued for five days. The solution was removed, the soil washed free of acid, and then again agitated with a further quantity of solvent. The calcium carbonate originally present was practically all removed in the first extraction, and no steps were taken to restore it. In the second extraction less than half the amount of phosphoric acid was removed, in the third about one-half that obtained in the second, and, finally, by the time of the sixth extraction the quantity removed by each successive treatment became constant.

Experiments were then made on the soil to which dicalcium phosphate was added, and it was ascertained that some of the phosphoric acid soluble in the citric acid was retained in the solid state by the soil. After a fourth and fifth extraction a point was reached where the compound remaining in the soil was uniform.

¹ *Trans.*, 1906, 89, 205.

But this point of equilibrium varied in different soils, indicating differences in the nature of the phosphoric acid compounds in soil. Whitney's theory of the formation in soils of solutions of approximately constant composition, and independently of the fertilisers used, is thus not supported, and it would appear that the soil water is of varying concentration in different soils. The available phosphoric acid is shown by the sum of the phosphoric acid removed in the first four or five extractions; but as this has a constant ratio to the amount dissolved in the first extraction of twenty hours, for all practical purposes a single extraction gives as good a result as repeated ones.

G. S. Fraps¹ states that aluminium, iron, and calcium phosphates (as in phosphorite, vivianite, apatite, &c.), dissolve completely in $N/5$ hydrochloric and nitric acids under soil conditions. Conducting pot experiments with cow-peas he found that the plants removed from 17 to 60 per cent. of the phosphoric acid soluble in nitric acid, and he concluded that a relation was indicated between the phosphoric acid so dissolved and the needs of the soil.

Potash and Soda.

M. Berthelot,² by treating wood ashes with 1 per cent. hydrochloric acid and then washing with water, found that from 5 to 6 per cent. of the total potassium was retained as organic compounds. He also ascertained the presence of organic potassium compounds in living vegetable tissues; if digested with potassium acetate solution the insoluble organic matter fixed a certain amount of potassium, and if solution of calcium acetate was used calcium was fixed and potassium liberated.

The influence of potassium manures on the quality of barley has been studied by several observers, and, among them, O. Reimer³ has noticed that, whilst potash increases the yield of grain, the amount of proteins is in no way reduced. K. Asō⁴ obtained the same increase of grain with barley by using potassium chloride, finding, however, that potassium sulphate was more favourable to straw production; potassium silicate was, on the whole, the best form, and the new potassium manure "martellin" gave good results in this connexion. Sulphate of potash and kainite have been compared as potassium manures for potatoes at the Woburn Experimental Farm,⁵ the results of 1905 confirming those

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 823.

² *Compt. rend.*, 1905, **141**, 793, 1182.

³ *Chem. Centr.*, 1906, i, 154.

⁴ *Bull. Coll. Agr. Tōkyō*, 1906, **7**, 67.

⁵ *J. Roy. Agric. Soc.*, 1906, **67**, 305.

previously recorded to the effect that sulphate of potash is, on a light, sandy loam, a preferable form to kainite, 1 cwt. per acre of the former and 4 cwt. per acre of the latter being respectively used. This proved to be alike the case whether nitrate of soda or sulphate of ammonia was used as the nitrogenous manure. The relations of potassium and sodium salts in soils and as supplied in manures have occupied considerable attention, and especially in connexion with sugar-cane and sugar-beet cultivation. J. F. Breazeale¹ grew wheat plants in solutions containing all necessary elements except potassium and sodium, then removing the plants to solutions with full nutrient constituents and ascertaining the amounts of the constituents taken up. In this way it was found that potassium was taken up much more vigorously when sodium had been left out in the first period than when it was present all the time. Similarly, by taking beet plants which had been first grown in soil to which potassium or sodium salts had been given as manures, and then removing them to solutions containing full nutrient matters, the plants to which no potassium had been given to the soil for some years took up potassium more vigorously than where sodium had been applied. J. Urban² has studied the relation of potassium and sodium salts in the case of sugar-beet. When sodium nitrate alone was used on a sandy humus soil there was abnormal development of leaf, and though the total ash (leaf and root) was much the same as in normal beets, it contained a very high proportion of sodium salts, much exceeding that of the potassium salts. So, although sodium may replace potassium in the plant's composition, it is at the expense of proper root development and consequently of sugar-production. Urban attributes the abnormal composition to the great preponderance of nitrogen over potash, the ratio of K_2O to N having been 1 : 3.1, whereas he considers that the best ratio for sugar production is 1 : 1.

Silica.

A. D. Hall and C. G. Morrison³ have examined again the part played by silica in the nutrition of plants, and, while confirming previous conclusions as to its not being a necessary constituent of plant food, have brought out interesting points as regards the functions which it exercises, and mainly in reference to the taking up of phosphoric acid. The observations have been made in respect of some of the permanent grass experiments in Rothamsted Park and the permanent barley plots in Hoos Field. On the grass land

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 1013.

² *Zeit. Zuckerind. Böhm.*, 1906, **30**, 397.

³ *Proc. Roy. Soc.*, 1906, **77**, B, 455.

the use of sodium silicate along with mineral manures and ammonium salts gives, over 42 years, an annual increase of 10 per cent. in the crop above that of a similarly manured plot without sodium silicate. An explanation of this is supplied by the barley plots, where sodium silicate has been employed with and without phosphates. Its use causes earlier formation of the grain and hastens the ripening of the crop. The omission of both silica and phosphoric acid results in a poor crop (27 to 28 bushels per acre), but if sodium silicate is applied without phosphoric acid the crop is increased to 34 to 36 bushels, and more phosphoric acid is found in the ash of the grain, although there is less in the ash of the straw. Silica would thus appear to be able partly to replace phosphoric acid, the effect of it being that it imparts a stimulus which enables more phosphoric acid to be taken up by the plant from the soil. Barley plants were examined at different stages of growth, and it was found that, in general, only 9 per cent. of the silica reaches the grain in the early stages, and that, whereas ordinarily the dry matter reaches its maximum about July 18-25, if no silica or phosphoric acid is supplied the dry matter does not reach its maximum until August 8. A series of water-cultures further confirmed these results and showed that while silica cannot replace phosphoric acid it may stimulate the plant to take up more. And, lastly, by extracting the soil of the different plots with hydrochloric and citric acid respectively it was shown that the sodium silicate has no direct solvent action on the soil phosphates.

The "Rarer" Constituents of Plants and Soils.

(a) Manganese.

N. Passerini¹ grew lupins (*Lupinus albus*) in a soil containing 0.068 per cent. of manganese, and examined the different parts of the plant in regard to their contents of manganese. The leaves contained 8.26 per cent. of ash, and of this ash 12.43 per cent. consisted of manganese reckoned as Mn_2O_3 ; the seed pods contained the next highest proportion, namely, 6 to 7 per cent. of the ash (total 3.5 per cent.), and then the stems and the seeds, the roots lastly having still less. In pot experiments, with and without addition of manganese carbonate, the soil containing only 0.0002 per cent. of manganese, the dry matter contained 0.0095 of manganese when none was added and 0.0636 per cent. when it was given as manure. T. Katayama² showed that manganese has a stimulative effect on oats, barley, rice, &c., although this is not so great

¹ *Bol. Ist. Agrar. Scandicci*, 1905, [ii], 6, 3.

² *Bull. Coll. Agric. Tōkyō*, 1906, 7, 91.

as on leguminous plants. Using manganous sulphate on peas in quantity to supply 0.015 per cent. manganous sulphate to the soil, the increase was 50 per cent. in the yield of straw and 25 per cent. in that of the seeds, whereas with barley the total increase was only 10 per cent. Quantities much exceeding the above tended to decrease the yield. G. Salomone¹ confirms these results as to the beneficial influence of a certain quantity of manganese and the tonic action of large amounts, and points out that the manganic salts are more tonic than the manganous, manganic acid especially being hurtful. M. Nagaoka² obtained confirmation of former experiments, getting with rice a gain of 15 per cent. when using manganese sulphate up to 100 kilos. per hectare.

(b) *Copper.*

A. Stutzer³ grew *Trifolium pannonicum* in pots with sand, garden soil, calcium carbonate, and mineral manures. He added to two of them finely-divided copper (1 gram and 10 grams) and to other two powdered copper oxide in the same amounts, other pots receiving no copper. In only one instance—when 10 grams of copper oxide were used—was any injury noticeable, but here the plants either failed or remained very small. Examination of the plants failed to detect copper in them, even in the roots. W. W. Skinner⁴ has examined the effect on vegetation of irrigation water containing copper salts derived from the waste products of mining operations. One part of copper in 800,000 has been found to be fatal to the growth of corn, and as little as one part in 700 millions will retard the growth of wheat seedlings. The author concludes that 1 part of copper per million is enough to condemn a water for use for irrigation purposes. He has further tested the general belief that the presence of carbonates and bicarbonates, by rendering copper insoluble, will remove any danger of injury, and finds that it is not justified, inasmuch as a considerable amount of copper remains in solution, even if carbonates and bicarbonates are present in quantity. E. Bréal⁵ treated seeds with a solution prepared by boiling starch in 1 litre of 0.3 per cent. of copper sulphate solution. The seeds were soaked for twenty hours and then left to dry. Their weight was increased somewhat, their germination was improved, and, besides the freedom from "smut" and other diseases, the crop was somewhat increased. (See also under mercury.)

¹ *Chem. Centr.*, 1906, ii, 532.

² *Bull. Coll. Agric. Tôkyô*, 1906, 7, 77.

³ *Landw. Versuchs-Stat.*, 1906, 65, 285.

⁴ *J. Amer. Chem. Soc.*, 1906, 28, 361.

⁵ *Compt. rend.*, 1906, 142, 904.

(c) *Aluminium.*

H. Micheels and P. de Heen¹ investigated the effect of aluminium salts on the germination of wheat, with the result that, whilst they find alumina or kaolin to be beneficial, the addition of soluble aluminium salts is proved to be injurious. On seedlings themselves it would seem, from the work of H. D. House and W. J. Gies,² that the injurious effect is dependent entirely on the extent of the concentration.

(d) *Mercury and Silver.*

T. Bokorny³ finds that algæ are killed by salts of copper, mercury, and silver if the concentration is 1 to 1 million. All other metals require to be in more concentrated solution than this to do any injury.

(e) *Iodine.*

S. Uchiyama,⁴ by using small amounts of potassium iodide, increased the yield of *sesamum* and spinach. With *sesamum* he obtained an increase of 16 per cent. by using 124 grams of potassium iodide per hectare. This was confirmed by a field experiment, and the matter has some interest owing to the common practice of using seaweed as manure where available.

(f) *Fluorine.*

Experiments of K. Asō⁵ with both soil and water culture seem to point to precipitated calcium fluoride as possessing some stimulating action. This cannot, however, be due to hydrogen fluoride, inasmuch as this is not liberated by carbon dioxide and weak acids.

Availability of Soil Constituents.

J. König, J. Hasenbäumer, and C. Coppenrath,⁶ in seeking for a method of determining the available constituents of soils, have obtained the best results by placing the soil in a linen bag inside a copper vessel and heating the whole with water for three hours under a pressure of four atmospheres. The solution is then filtered, evaporated down, and the different constituents estimated.

¹ *Bull. Acad. roy. Belg.*, 1905, 520.

² *Proc. Amer. Physiol. Soc.*, 1905, xix—xx.

³ *Chem. Zeit.*, 1905, 29, 1201.

⁴ *Bull. Imp. Centr. Agric. Exp. Stn. Japan*, 1906, 1, 35.

⁵ *Bull. Coll. Agr. Tōkyō*, 1906, 7, 85.

⁶ *Landw. Versuchs-Stat.*, 1906, 63, 471.

Oxidation in Soils.

E. J. Russell¹ has continued his work on the rate of oxidation in soils and the relation this bears to their productiveness. Oxidation is due mainly, but not exclusively, to the action of microorganisms, as it still goes on when the soil has been sterilised by heating or by treatment with mercuric chloride or other reagents. The rate of oxidation is, however, much reduced. Moreover, it does not depend on the amount of organic matter present; up to a point the presence of moisture helps; similarly, the presence of calcium carbonate or of a carbohydrate aids the rate. With partial sterilisation the rate of oxidation also increases, and this would lead to the belief that, whilst the work of some organisms is checked, the activity of others may be favourably influenced by partial sterilisation. This only takes place, however, under aerobic conditions, as in arable soils, but not in pasture soils, where the conditions are anaërobic.

C. Schulze² has investigated the effect of sterilisation of soils, and finds that whilst some substances injurious to plants are formed, the soil constituents generally are made more available. The result as regards the plant will depend on the predominance of one or the other influence.

It is clear from the foregoing and the observations of others, that there remains still a great deal of work to be done in ascertaining exactly what changes take place in the bacterial and chemical conditions of different soils as well as in their physical relations, through the employment of processes of sterilisation, partial or complete, and that the results obtained with sterilised soils have to be taken in conjunction with the various changes thereby produced.

Germination.

P. Becquerel³ has studied the action of carbon dioxide on seeds which have been decorticated or perforated. When the seeds are in their naturally dry condition they will not be injured, though kept in an atmosphere of carbon dioxide; but if they are previously immersed in water for a quarter of an hour they will be all killed by exposing them to an atmosphere of carbon dioxide. O. Kamberský,⁴ by placing seeds for forty-eight hours in contact with a nutritive solution containing ammonium nitrate, potassium

¹ *Brit. Assoc. Reports* (Section B), York, 1906.

² *Landw. Versuchs-Stat.*, 1906, **65**, 137.

³ *Compt. rend.*, 1906, **142**, 843.

⁴ *Chem. Centr.*, 1906, i, 570.

nitrate, di-ammonium hydrogen phosphate, and di-sodium hydrogen phosphate (Iszleib's solution), found that germination was retarded and a lower germination percentage obtained. A. Stutzer¹ has shown also that nitrates generally act injuriously on germinating seeds; beet plants are very sensitive to nitrates, but red clover resists their action. The behaviour of cyanamide towards germinating seeds has already been dealt with (page 261), but Bartsch² has shown that, while the germination of mustard, oats, and barley is affected when the seeds are sown at the time of applying the cyanamide, and will be still noticeable if a week intervenes, yet, if an interval of three weeks is allowed between the application of the cyanamide and the sowing of the seed no injurious action will follow.

H. Micheels and P. de Heen³ have further found that ozone has an injurious effect on seedlings, the roots in particular being attacked.

Assimilation.

F. L. Usher and J. H. Priestley⁴ show that, in presence of chlorophyll and under suitable conditions, aqueous carbon dioxide is decomposed into formaldehyde and hydrogen peroxide, formic acid being produced as an intermediate substance. This goes on independently of any enzyme action, and depends solely on the proper physical and chemical conditions being present. It is possible to reconstruct this process outside the green plant. The formaldehyde and hydrogen peroxide rapidly undergo change, and are not found in the assimilating leaf under ordinary conditions. Working on the leaves of *Acer Negundo*, B. Schultze⁵ ascertained that the increase in weight of the leaves, under the influence of light, was not due only to the assimilation of starch, but also to that of proteins. But while carbon assimilation went on the production of proteins gradually diminished.

Development.

By growing green plants without carbon dioxide in an artificial soil containing amides, J. Lefèvre⁶ showed that the dry matter of the plants rapidly increases, the growth being quite normal. In absence of light the plants failed altogether, although amides were present. The results go to show that the carbon dioxide of the soil is not absorbed by the roots, or, at least, is not utilised by them.

The oxidising power of living cells on the surface of roots was

¹ *J. Landw.*, 1906, **54**, 125.

² *Chem. Centr.*, 1906, i, 585,

³ *Bull. Acad. roy. Belg.*, 1906, 364.

⁴ *Proc. Roy. Soc.*, 1906, **78**, B, 318.

⁵ *Bied. Centr.*, 1906, **35**, 35.

⁶ *Compt. rend.*, 1905, **141** 664, 834, 1035.

shown by experiments of M. Raciborski,¹ who grew plants in solutions which do not affect the life of the roots' cells, but which, on oxidation, yield products either themselves coloured or capable of colouring suitable reagents. This power is, however, a purely local one, and is confined to the absorbent surfaces of the roots, being strongest near the root hairs.

The influence of light on the development of proteins in the wheat grain has been studied by J. Dumont.² The accumulation was greatest under the influence of brown light, then under green, blue, and red light successively. In the absence of light, A. Kiesel³ found not only asparagine to increase, but also other amino-acids, especially leucine, and certain bases, such as arginine, not found in healthy plants.

H. Schjerning,⁴ in investigating the formation and changes in the protein substances of barley during growth, ripening, and storing, concludes that barley has attained its full maturity when the soluble carbohydrates are converted into insoluble ones and the soluble into insoluble proteins. H. T. Brown, F. Escombe, A. McMullen, and J. H. Millar⁵ have observed the migration of nitrogen in barley from the endosperm to the embryo during germination. It was noticed by them that if the embryo was removed and allowed to grow in water or in a carbohydrate medium the root exhibited a restricted development, and the embryo seemed to be suffering from nitrogenous starvation. This nitrogen it would, in the ordinary course, derive from the endosperm. The observation was continued to barley undergoing the malting process, the nitrogen being determined at various intervals in the endosperm, embryo, rootlets, &c. It was found that after nine days' germination 35 per cent. of the nitrogen originally present in the endosperm had migrated to the embryo, and must in so doing have been converted from the insoluble protein form into soluble and diffusible compounds.

The same authors continued their studies on the nitrogenous constituents of malt that are soluble in cold water, with a view to ascertaining how far the quality of barley depends on these. An examination of the sprouted "culms" led to the identification in them of asparagine, allantoin, betaine, and choline. The water-soluble uncoagulable nitrogens of malt have now been divided by the authors into six classes of bodies, and their approximate percentages have been also worked out. They consist of the

¹ *Bull. Acad. Sci. Cracow*, 1905, 338.

² *Compt. rend.*, 1905, 141, 686.

³ *Zeit. physiol. Chem.*, 1906, 49, 12.

⁴ *Trav. Laborat. Carlsberg*, 1906, 6, 229.

⁵ *Trans. Guinness Research Lab.*, 1906, 1, part 2, 149, 169, 175, 238, 242, 284, 338.

following:—ammonia-nitrogen, 3·5 per cent; malt-albumose nitrogen, 20 per cent.; malt-peptone nitrogen, 31 per cent.; amide and amino-nitrogen, 8·5 per cent.; nitrogen due to organic bases, 4 per cent.; uninvestigated bodies, 33 per cent. The conclusion is also arrived at that, from the chemical point of view, no distinction can be drawn between animal and plant proteins.

The action of light on the transformation of sugars in young plants has been studied by W. Lubimenko¹ in connexion with the embryos of *Pinus pinea*. When these were exposed to light of varying intensity in sterilised solutions of sucrose, dextrose, maltose, lactose, galactose, and arabinose, it was found that under the action of the light the absorption of sucrose, dextrose, and arabinose went on, but with varying activity, diminishing as the intensity of the light increased. The light had no effect on the assimilation of maltose, lactose, lævulose or galactose.

According to G. A. Calabresi² pentosans would seem to be formed in young plants, but to decrease later on. In sugar-beet, when pentosans are high in amount sucrose is low, and, generally, in plants the pentosans are higher when nutritive constituents are low.

W. Palladin and S. Kostytschew³ show that during the anaërobic respiration of seeds and seedlings a considerable amount of alcohol is formed. Both living and frozen seeds have been experimented with; with frozen peas alcohol is formed whether oxygen be present or not, but with living peas the formation of alcohol only goes on in absence of oxygen. Acetone is also found to be formed during anaërobic respiration.

W. D. Bigelow, H. C. Gore, and B. J. Howard⁴ have investigated the changes which go on during ripening in certain plants containing a good deal of tannin. They find that the tannin disappears during the ripening, passing possibly into insoluble forms. Microscopical examination shows that at first the tannin is fairly uniformly distributed through the fruit, but that, as ripening proceeds, it becomes deposited in insoluble form in special cells.

Micro-organisms.

N. L. Söhngen⁵ was led, by the consideration that methane, although so abundantly produced, is yet found only in traces in the atmosphere, to search for organisms which were capable of feeding on the hydrocarbon. He found that if a culture-liquid

¹ *Compt. rend.*, 1906, **143**, 516.

² *Chem. Centr.*, 1906, ii, 964.

³ *Zeit. physiol. Chem.*, 1906, **48**, 214.

⁴ *J. Amer. Chem. Soc.*, 1906, **28**, 688.

⁵ *Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 327.

was impregnated with garden soil, sewage or the like, in an atmosphere of methane and oxygen at 38° , a slimy, pink film formed on the surface, and that this consisted of short, rod-like bacteria, which he named *Bacillus methanicus*. Within a week the methane is nearly all absorbed, being thus utilised as a source of carbon. H. Kaserer,¹ working on the same subject, shows that the presence of hydrogen and methane hinders the production of nitrites from ammonium salts. If there is a plentiful aëration, both oxidation of hydrogen and nitrification may go on together, but, if aëration be imperfect, nitrification will only begin after all the hydrogen has been oxidised. V. Omeliansky² finds that methane is produced by fermentation from cellulose, gelatin, peptone, and many other substances, and thinks it probable that all soils that have organic matter will produce methane. Accordingly, it is not possible to say, from the mere fact of methane being produced, what the nature of the organic matter decomposed is. From the excrements of pigeons C. Ulpiani and M. Cingolani³ have isolated a micro-organism which decomposes guanine into carbamide, guanidine, and carbon dioxide.

In the fermentation of sugar-cane juice C. A. Browne⁴ has noticed that a frequent fermentation is that resulting in the formation of cellulose. This he has investigated and finds it to be aërobic, being due probably to *Bacterium xylinum*. From cane juice the amount of cellulose thus formed may be 7 per cent. of the total sugar fermented.

The effect of light on bacteria has been investigated by H. Thiele and K. Wolf.⁵ While the bacteria were destroyed quickly by strong light, if the light was filtered through solutions of nitrates or oxalic acid it had no effect on the bacteria; if passed through disodium phosphate and potassium thiocyanate solutions enough active light passed through to kill the bacteria. From this the active bactericidal region was fixed. Light filtered through a piece of blue rock-salt crystal (the ultra-violet rays alone passing through) rapidly destroyed the bacteria.

W. Hoffmann⁶ has observed the action of carbon dioxide at high pressure on the bacteria contained in river water and in milk. Under a pressure of 50 atmospheres the bacteria are killed entirely in twenty-four hours in the case of river water. But with milk the bacteria are not entirely destroyed, even at a temperature of 50° , although the casein is coagulated and separates out.

¹ *Centr. Bakt. Par.*, 1905, ii, 15, 573.

² *Ibid.*, 1906, ii, 15, 673.

³ *Atti R. Accad. Lincei*, 1905, 14, ii, 596. ⁴ *J. Amer. Chem. Soc.*, 1906, 28, 453.

⁵ *Arch. Hygiene*, 1906, 57, 29.

⁶ *Sixth Int. Congr. Appl. Chem., Chem. Zeit.*, 1906, 30, 422.

Enzymes.

J. Stoklasa¹ has isolated several enzymes from beetroot. These he identified as oxydases, invertase and glycolytic enzymes. The latter set up alcoholic fermentation in dextrose solutions, alcohol and carbon dioxide, as well as small quantities of acetic and lactic acids being produced. Formic acid has also been found as a product, and the author hints that this may give rise to the hydrogen which is evolved together with carbon dioxide, and may play a part in the assimilation of carbon in the chlorophyll cells, in which process formaldehyde and water are formed. The glycolytic enzymes are given as (a) lactolase, (b) alcoholase, (c) acetolase (d) formilase, these causing the production of lactic acid, alcohol, acetic acid, and formic acid respectively.

C. A. Browne² finds invertase in the green tops of sugar-cane, and notes that if the tops are removed when the cane is cut the diffusion of the enzyme into the stalk is prevented, and there is less loss of sucrose. The darkening which sugar-cane juice undergoes after expression is due to oxydases.

Glucosides and Cyanogenesis.

Several investigators have continued their inquiries into the presence in various plants of certain glucosides which, under the action of an enzyme, gives rise to the production of hydrocyanic acid. Numerous plants other than *Phaseolus lunatus* (with which Dunstan and Henry worked) have been found to contain glucosides of this character, and the yield of hydrocyanic acid has been quantitatively recorded. W. R. Dunstan, T. A. Henry, and S. J. M. Auld³ find *phaseolunatin* in small amount in flax seed, and an enzyme of the emulsin type similar to that in *Phaseolus lunatus*. They also find a glucoside and an enzyme similar to, if not identical with, those of *Phaseolus lunatus*, in the root of bitter cassava. L. Guignard⁴ also establishes the presence of cyanogenetic glucosides in many of the Rosaceæ. He has further determined the amount of hydrocyanic acid obtained from the ground beans of *Phaseolus lunatus*, obtaining 0.052 to 0.102 per cent. with Java beans, but considerably less with Burmah, Madagascar, and Provence varieties. Further, he does not find, as others have done, that the white cultivated beans are quite free from hydrocyanic acid, and, in

¹ *Sixth Int. Congr. Appl. Chem., Chem Zeit.*, 1906, **30**, 422.

² *J. Amer. Chem. Soc.*, 1906, **28**, 453.

³ *Proc. Roy. Soc.*, 1906, **78**, B, 145 and 152.

⁴ *Compt. rend.*, 1906, **143**, 451, and **142**, 545.

examining white beans that occur among Java beans he obtains just as much hydrocyanic acid from them as from coloured beans. He states that the poisonous properties are not removed on boiling, as this only destroys the enzyme and not the glucoside. R. R. Tatlock and R. T. Thomson¹ obtained from Java beans from 0.027 to 0.137 per cent. of hydrocyanic acid. They examined separately the variously coloured beans, but could arrive at no generalisation as to the relation of colour to yield of acid. Discussing the statement that has been made that cyanogen is in the husk and not in the kernel, they state that this is not the case, but that the kernel has ten times as much as the husk. They examined several different varieties of beans, but only found hydrocyanic acid to be produced from Java beans and Rangoon beans. On steeping the beans in warm water and boiling them thoroughly, an original percentage of 0.009 of hydrocyanic acid falls to 0.002 and the enzyme is destroyed; in cold water the cyanogenetic glucoside is decomposed.

Kohn-Abrest² disagrees with the conclusion of Dunstan and Henry that there is one cyanogenetic glucoside in *Phaseolus lunatus*, and considers that many are present. J. W. Leather³ examining a sample of *sorghum* (*Sorghum vulgare*) fodder which had proved harmful to cattle in India, found it to be immature and to contain 1.28 grains of hydrocyanic acid per lb. of green stuff. The largest quantity was found in the leaves. If left to mature the plant contained no hydrocyanic acid, but drying the immature fodder in the sun produced no change in quantity. The glucoside present was *dhuririn*, as previously recognised by Dunstan and Henry. Leather confirms the presence of hydrocyanic acid in Rangoon beans and immature linseed.

Foods and Feeding.

K. Farnsteiner, K. Lendrich, and P. Buttenberg⁴ examined lards obtained from pigs that had been fed on potatoes, maize meal, cotton-seed meal, &c., with the result that a portion of the oil derived from the foods was shown to be deposited in the body fat of the animal. This was especially marked in the case of maize meal. The decomposition of foods in the absence of air has been investigated by J. König, A. Spieckermann, and H. Kutteneuler,⁵ who find it to be practically the same in nature as when oxygen is present, although the products are different in quantity. The greatest loss is in the non-nitrogenous extract, although when air

¹ *Analyst*, 1906, **31**, 249.

² *Compt. rend.*, 1906, **143**, 182.

³ *Agric. J. of India*, 1906, **1**, 220.

⁴ *Zeit. Nahr. Genussm.*, 1906, **11**, 1.

⁵ *Ibid.*, 1906, **11**, 177.

is absent there is comparatively little loss of dry matter. The loss of nitrogen is very small, the proteins decomposing only slightly. The foods, in absence of air, tend to become strongly acid, but do not alter their appearance.

E. Schulze,¹ taking potatoes, as containing a relatively large amount of asparagine, shows that this is converted, when consumed by animals, into amino-acids and then into succinic or malic acids, which have no value for fat production in the case of carnivorous animals. O. Kellner,² however, from experiments with sheep, concludes that asparagine may indirectly economise proteins in the case of ruminants. Lactic acid he finds to be simply oxidised and to produce heat only.

J. König³ has attempted to separate the various constituents making up the so-called "crude fibre" in foods, and gives methods of ascertaining the cellulose, lignin, and cutin. Lignin is separated by digestion in the cold with hydrogen peroxide in presence of aqueous ammonia, it being converted by this treatment into soluble products. Cellulose is next separated from cutin by treatment with copper-ammonium hydroxide, it being thereby dissolved, leaving the cutin undissolved. As the plant gets older the lignin increases more than the cellulose, and, broadly speaking, the higher the percentage of lignin and cutin the lower is the digestibility of the crude fibre.

J. Hendrick,⁴ following up the work of T. B. Wood, R. A. Berry, and S. H. Collins (see *Annual Report*, 1905, 264) has obtained similar results for yellow swedes and turnips grown in the N.E. of Scotland. He finds marked variations according as the roots are grown in different parts of the country, and emphasises (as did the authors named) the necessity of taking a large number of roots (100 suggested) in order to get satisfactory results. He has made the attempt to arrive at the value of the roots by comparing the ratio of the soluble to the insoluble matter in the solid matter of the roots.

Crops.

(a) "*Strength*" in *Wheat*.

This subject has been further attacked both from the chemical and the biological side. A. D. Hall⁵ has examined critically the different constituents of the grain, with the view of finding out to which of them the quality of "strength" may be due. But he does not find any consistent correspondence between the pre-

¹ *J. Landw.*, 1906, **54**, 65.

² *Bied. Centr.*, 1906, **35**, 45.

³ *Zeit. Nahr. Genussm.*, 1906, **12**, 385.

⁴ *Trans. High. and Agric. Soc. of Scotland*, 1906.

⁵ *Rep. Home-grown Wheat Committee (Millers' Gazette)*, 1906.

dominance of any of these and the possession of "strength," and is unable to go beyond the general statement that nitrogen may, as a rule, be taken as a test of "strength," whilst the carbohydrate matters do not contribute to it. Hall finds that different stages of ripeness do not determine "strength," inasmuch as a crop cut dead ripe may be just as "strong" as one cut green. Nor does it follow that a highly nitrogenous grain is of necessity a "strong" one; some were, indeed, the weakest of all from a baker's point of view. But it was observed that these, if kept, became changed; their physical structure seemed to be altered, and they were then increased in "strength." Hall remarks on the observed "acidity" of flour, and finds that this is due to the presence of a little potassium phosphate.

Meanwhile the subject has been investigated further from the biological side by R. H. Biffen¹ and with more hopeful prospects. Biffen eliminates climatic conditions as having little or no bearing on the question, and attributes the whole to the matter of "selection," and looks to the producing of "hybrids" to obtain the desired quality of "strength" combined with good yield.

(b) *Quality in Barley.*

The results obtained at the Woburn Experimental Farm for the years 1898—1904 on the influence of manures as affecting the yield and quality of barley have been collected and summarised,² and, in general, confirm the results obtained at the Rothamsted Experimental Station. The main points as regards quality are that this was improved by mineral manuring (superphosphate with sulphates of potash, soda, and magnesia), that farmyard manure gave very variable results, and that the best ones were obtained with mineral manures in combination with ammonium salts or nitrate of soda used in moderate quantities. Nitrate of soda by itself or used in excess gave a low "weight per bushel" and much "tail" corn.

Industries.

(a) *Sugar.*

A considerable impulse has been given of late to the growing of sugar, more particularly of cane-sugar, and with this has come an extension of inquiry into points connected with the cultivation of the crop and the securing of the produce.

H. W. Wiley³ summarises his observations on the influence of environment on sugar production in the beet. Temperature he

¹ *J. Agric. Sci.*, 1907, 2, 1.

² *J. Fed. Inst. Brewing*, 1906, 12, 408.

³ *U.S.A. Dept. Agric. Bull.*, 1905, 96.

finds to be of the greatest importance; there is little relation between sunshine and sugar yield, but longer daylight means more sugar; rainfall only incidentally affects the output, but a small yield of crop means an increased sugar percentage; lastly, the juice becomes purer as the percentage of sugar rises.

H. and L. Pellet¹ find that sucrose is not uniformly distributed through the beetroot; some cells contain only water and salts, and the water is that termed by Scheibler "colloidal" water. Hence the difficulty in obtaining representative samples. Complete diffusion of the juices only takes place when the pulp is finely ground and digested with cold water or hot alcohol.

K. Andrlik and J. Urban² have examined the "objectionable" nitrogenous constituents in beet-root juice, and find that these are not amide or ammonium compounds. About 70 per cent. of the whole of the injurious matters originally present in the root are found in the juice. This quantity is increased by storage of the roots, probably owing to a breaking-down of the proteins.

Experiments in sugar-beet growing in the eastern counties of England³ have given in 1906 an average yield per acre of fourteen tons of roots, containing 16 per cent. of sugar, with a coefficient of purity 87. This yield, however, is not sufficient, in the circumstances of this country, to "pay" for the manufacture of sugar. W. D. Horne⁴ has inquired into the deterioration which sugar-cane undergoes when the canes have been cut. On each of six successive days he cut off pieces from canes, and noticed that the deterioration was greater with the top part of the cane than the bottom, but there was also a deterioration due to keeping. Thus, starting with 16.97 per cent. of sucrose on the first day, by the time the fifth day was reached the sucrose had fallen to 11.86 per cent.; in the first day there was a deterioration of 0.25 per cent., in the next two of 1.75 per cent., and in the next two of nearly 4 per cent. F. Watts and H. A. Tempany⁵ observed the changes which sugar-cane juice undergoes when allowed to ferment spontaneously; the juice becomes acid and of a yellow colour, a dark scum rising to the surface; alcoholic fermentation sets in, carbon dioxide is given off, and quite 8 per cent. of alcohol is formed. Then acidification of the alcohol ensues, "cane sugar" being obtained. The acidification of the juice was found to be produced by oxidation of the sugar by bacterial agency; this could be prevented by the addition of 2 per cent. of phenol to the juice.

¹ *Bull. Assoc. Chim. Sucr. Dist.*, 1906, **24**, 615.

² *Zeit. Zuckerind. Böhm.*, 1906, **30**, 282.

³ *Rep. E. Suffolk Chamber of Agriculture*, 1907.

⁴ *J. Soc. Chem. Ind.*, 1906, **25**, 161.

⁵ *West Ind. Bull.*, 1906, **6**, 387.

C. A. Browne,¹ jun., attributes the gradual inversion of the sucrose after the cane has been cut to the invertase which exists in the green tops of the cane. He has investigated the different fermentations, aërobic and anaërobic, which take place in the juice. Among the former are those due to *Bacterium xylinum* and to *citromyces*, and among the latter that produced by *Leuconostoc*, a viscous fermentation.

H. Pellet² refers to the suggestion of adding invert-sugar to molasses to aid crystallisation of the latter, since sucrose is less soluble in invert-sugar solution than in water, but he shows that this is not an advantage, inasmuch as the invert-sugar brings about the retention of more water, and this more than neutralises the benefit that might accrue.

(b) Tea.

H. H. Mann³ in a paper entitled "The Fermentation of Tea" (part I.) gives a valuable contribution to our scientific knowledge of the manufacture of tea. Indeed, it may be taken, in conjunction with his earlier paper, "The Ferment of the Tea Leaf" (see *Annual Report*, 1904, 215) as supplying the first clear exposition of the scientific side of the subject. Moreover, it affords a most useful example of how the study of the underlying chemical principles can be made to contribute to the practical well-being of an important industry. Mann had shown in his earlier paper that the fermentation is due to an enzyme of the nature of an oxydase, and that the quantity in which it is present is an indication of the quality of the tea. He now goes on to consider the various constituents of the leaf, to observe the changes in them during the different processes of withering, rolling, &c., and to see in what way these affect the value of tea as a finished product. Living organisms, it is shown, do not take part in the fermentation, and their exclusion as far as possible from the fermenting room should be secured. The constituents studied in detail are (1) essential oil, (2) caffeine (or theine), (3) tannin. The quantity of essential oil present is very small; it is driven off at a high temperature, and changes into a resin on exposure to air; it seems to be one of the chief factors in determining flavour in tea. Caffeine exists to the extent of 3 to 5 per cent. Its presence has no bearing on the market value of tea, although it may have on its medical value. Mann next deals very fully with the matter of tannin, and shows that, contrary to general opinion, this is not an objectionable feature, but that there is a close connexion between the quantity

¹ *J. Amer. Chem. Soc.*, 1906, **28**, 453.

² *Bull. Assoc. Chim. Sucr. Dist.*, 1906, **24**, 669.

³ *Indian Tea Assoc.*, 1906, **1** and **2**.

of tannin that can be removed in a five minutes' extraction with boiling water and the value of tea in the market. Tannin, as it occurs in the leaf, seems to be combined with sugar, and the tannin undergoes oxidation during fermentation of the leaf, through the presence of the oxidising enzyme. The oxidised tannin will then combine with the caffeine and other materials to form fresh substances which are mostly insoluble in water. During the process of rolling, the soluble matter in the leaf is reduced, and so is the amount of soluble tannin. Mann has further noticed the influence of light on the fermentation of tea, and finds that, whilst fermentation proceeds rather less rapidly with a blue light, there is no change in the percentage of tannin, but only in that of total soluble matter. What is of importance, however, is thickness of spreading, and this should not exceed $1\frac{1}{2}$ inches in depth. Experiments in green-manuring for tea established the usefulness of leguminous plants, especially *sau* (*Albizzia stipulata*).

(c) *Tobacco*.

J. Toth¹ has set out a new method of determining the organic acids in tobacco. Expressing these in terms of oxalic acid, he finds the quantity to range from 3.6 to 8.7 per cent., and, after trials with 32 different samples, concluded that bad-burning tobacco was that which contained the most organic acids, and *vice versâ*.

(d) *Cinchona*.

D. Howard² shows that by careful selection and cultivation the amount of quinine alkaloid in cinchona bark has been raised in Java from 4 per cent. to 10 per cent.

(e) *Cassava*.

H. H. Cousins³ has estimated the amounts of starch obtained at different periods of growth from 23 varieties of cassava, grown in Jamaica. He gives the produce of starch per one-tenth acre as follows:—At 12 months, $3\frac{1}{2}$ tons; at 15 months, $5\frac{1}{2}$ tons; at 21 months, $7\frac{1}{4}$ tons.

(f) *Eggs*.

J. Hendrick⁴ has examined the composition of eggs preserved by the use of "water-glass"; he finds that there is a slow deposition of silica in the shell, but that there is no change in the composition of the interior portion.

¹ *Chm. Zeit.*, 1906, **30**, 57.

² *J. Soc. Chem. Ind.*, 1906, **25**, 97.

³ *Jamaica Gazette*, Nov. 22nd, 1906, 330.

⁴ *J. Agric. Sci.*, 1907, **2**, 100.

(g) *Milk.*

H. D. Richmond¹ gives his annual statement of the composition of milk, as obtained from good dairy farms supplying milk daily to London, during 1905. The figures are taken from an average of nearly 15,000 samples, and are as follows:—Fat, 3·73 per cent; solids-not-fat, 8·97 per cent.; total solids, 12·70 per cent.; sp. gr., 1·0323. The average percentage of fat of the morning milk alone was 3·54; of the evening milk, 3·91. These figures differ but very slightly from those of 1904.

A. Morgen, C. Beger, and G. Fingerling² have investigated, over a period of six years, the effect of adding fat, protein matter, carbohydrates, &c., to foods deficient in these several constituents. By adding fat they found the yield of milk and the amount of fat in it to be both increased, but by adding protein matter only the yield was affected favourably, but not the fat. The yield of milk was, however, increased more by adding a protein than by the addition of fat. The addition of carbohydrates also had no effect on the production of milk-fat. The authors conclude that fat alone has a specific action on the production of milk-fat. Further experiments with emulsified fats showed these to possess no advantage.

Von Soxhlet³ has observed the coagulation taking place in the case of milk that is faintly acid. At first a coagulum is formed on boiling, and this takes place when only one-eighth of the acid necessary to produce coagulation at the ordinary temperature is present. The coagulation is due to the formation of an insoluble compound of caseinogen and calcium salts.

F. Bordas,⁴ by exposing milk to an atmosphere containing formaldehyde, has found that air containing as little formaldehyde as 1 part in 100,000 will give the reaction for formaldehyde, although the milk may have been exposed for only a few minutes.

J. AUGUSTUS VOELCKER.

¹ *Analyst*, 1906, **31**, 176.

² *Landw. Versuchs-Stat.*, 1906, **64**, 93, 249.

³ *Chem. Centr.*, 1906, i, 579.

⁴ *Compt. rend.*, 1906, **142**, 1204.

MINERALOGICAL CHEMISTRY.

It is impossible to begin a report on the progress of Mineralogical Chemistry during the past year without making brief reference to the great loss this branch of science has sustained in the untimely death of S. L. Penfield. Equally happy as a theorist and as an experimenter, he has left in his work an enduring monument behind him. A sympathetic biographical notice, accompanied by a bibliography, has been contributed by L. V. Pirrson¹ to the pages of the *American Journal of Science*. In the person of H. A. Ward, America has also lost a veteran who, by his untiring energy as a collector, did good service in advancing our knowledge of meteorites. By the death of W. Meyerhoffer at the early age of forty-two, van't Hoff has been deprived of a fellow-worker and our science of one who did much to introduce to mineralogists and petrologists those ideas and methods of physical chemistry, the application of which promises such rich results in the future. It is, in fact, along these lines that the most important work has been done during the past year, and it is therefore fitting that this branch of the subject should occupy the first place in our survey.

General and Physical Chemistry of Minerals.

Salt Deposits.—J. H. van't Hoff² and his pupils have carried on their investigations with unabated energy. Number xlvi of the "Researches on the Formation of Oceanic Salt Deposits" appeared early in the year, and was devoted to a discussion of the conditions of occurrence at 83° of anhydrite, CaSO_4 , syngenite, $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, glauberite, $\text{CaNa}_2(\text{SO}_4)_2$, and penta-salt, $\text{Ca}_5\text{K}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$; the formation of calcium chloride and tachhydrite, $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, were also considered. In number xlvii the examination of the naturally occurring calcium compounds was brought to a conclusion by a study of the relations at 83° of the triple sulphates, polyhalite, $\text{Ca}_2\text{K}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, and krugite, $\text{Ca}_4\text{K}_2\text{Mg}(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$.

Work on the borates was begun last year, and the relations of

¹ *Amer. J. Sci.*, 1906, [iv], 22, 353.

² *Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 218, 412, 566, 653, 689.

tincal and octahedral borax elucidated. The more difficult and complex problem presented by the double borates of calcium and magnesium with a univalent ion has now been attacked, and the range of existence and the dissociation of $\text{NaCaB}_5\text{O}_{13}\cdot 8\text{H}_2\text{O}$ boronatrocalcite fully determined.

It has been shown in number *xlvi* that this substance splits into the individual borates at about 85° , and that it probably was not formed in nature at a temperature higher than 70° . Incidentally pandermite, $\text{Ca}_8\text{B}_{20}\text{O}_{33}\cdot 15\text{H}_2\text{O}$, was prepared artificially for the first time, together with a new substance, tricalcium borate, $\text{Ca}_3\text{B}_{10}\text{O}_{13}\cdot 9\text{H}_2\text{O}$, not as yet observed as a mineral. The mutual transformations of the hydrates of calcium monoborate, CaB_2O_4 , are the subject of a separate paper; and number *xlix* of the series is concerned with the conditions for the artificial preparation of colemanite, $(\text{CaO})_2(\text{B}_2\text{O}_3)_3\cdot 5\text{H}_2\text{O}$, which it is shown can be formed from the corresponding heptahydrate and sodium chloride at 83° , or from boronatrocalcite in the same medium at 70° .

Mutual Relation of Fused Silicates.—The past year has witnessed great activity in this line of research, and the entry of American workers into the field has resulted in a notable increase of our knowledge of the calcium and magnesium silicates. In the first place, E. T. Allen and W. P. White¹ have succeeded in preparing artificial wollastonite having properties identical with those of the natural mineral, and have also made a careful examination of the hexagonal calcium metasilicate, termed by them *pseudo-wollastonite*, and of the relations between these two substances. They find that wollastonite can be readily obtained from the glass made by melting, together, at a temperature of over 1500° , molecular proportions of quartz and calcium carbonate in a platinum crucible, which is then rapidly chilled by placing it in water. On heating this glass to about 800° to 1000° it crystallises directly and rapidly into wollastonite, identified by its optical characters. The specific gravity is 2.915. When heated to about 1180° wollastonite changes into pseudo-wollastonite. This change is an enantiotropic one, and under proper conditions reversible. The point of transformation was determined by heating wollastonite in contact with the other form for definite periods at various temperatures, and also by observing the rate of rise of temperature as heat was supplied to the mass, a slight absorption of heat being noticed at the transition point. The volume change accompanying the transformation is so slight that it is doubtful which is the denser form. The reverse transformation is not so easily effected, and does not take place when the two forms are merely heated in contact at temperatures between 900° and 1100° , even if the

¹ *Amer. J. Sci.*, 1906, [iv], 21, 89.

heating be continued for many hours. It can, however, be brought about by the aid of a solvent. Calcium vanadate proved suitable, and it was found that the change into wollastonite was complete if 5 grams of the silicate were heated with 1 gram of the vanadate for some days at a temperature of 800° to 900° . Beautiful transparent crystals were produced in this way. Analysis proved them to be nearly pure CaSiO_3 , and the mean specific gravity 2.913, crystallographic characters¹ and optical properties, agreed with those of wollastonite. This inversion also takes place readily in mixtures containing excess of lime or silica, as shown by Day and Shepherd. Pseudo-wollastonite is usually considered to be hexagonal, but F. E. Wright, who has made a careful optical study of Allen and White's preparations, thinks that it is more probably pseudo-hexagonal, its real symmetry being that of the monoclinic system. The melting point is 1512° , and on cooling the liquid almost invariably crystallises above 1200° as pseudo-wollastonite. The fact that the transformation takes place at 1180° has an important geological bearing, for it fixes an upper limit of temperature above which wollastonite cannot possibly have been formed, and neither pseudo-wollastonite nor paramorphs of wollastonite after pseudo-wollastonite have been met with in nature.

The work on wollastonite has been extended by A. L. Day and E. S. Shepherd² to embrace the whole series of combinations of lime and silica. They began by studying the properties of the two oxides. The melting point of lime is too high for any satisfactory measurements to be made. It can, however, be fused in the electric furnace, and on cooling crystallises with well-marked cubic structure. The mean specific gravity is 3.316 at 25° . Silica, either in the form of quartz, glass, or precipitated silica, when heated for a sufficient length of time at temperatures above 1000° , changes into tridymite. The change proceeds most rapidly in the case of the precipitated silica, a fine state of division being favourable to the transformation. In order to determine the transformation temperature as accurately as possible, quartz-glass was heated with vanadic acid, sodium tungstate, or a mixture of 80 per cent. potassium chloride with 20 per cent. lithium chloride. Below 760° quartz crystals were obtained. At 800° and higher tridymite was the only product. Inversion occurs therefore at about 800° , and the melting point of silica is really the melting point of tridymite, although by very rapid heating quartz can sometimes be melted without first changing into tridymite. Owing to the viscosity of the substance, it is exceedingly difficult to fix this point, but it seems probable that pure silica begins to melt at about 1600° .

To obtain a general idea of the behaviour of mixtures of lime and silica, small portions of finely-ground mixtures of known com-

¹ Two crystals were measured.

² *Amer. J. Sci.*, 1906, [iv], 22, 265.

position were placed in a row on platinum or iridium strip. The strip was gradually heated electrically and the order of melting noted. In this way two compounds and three eutectics were discovered. Mixtures containing more than 75 per cent. or less than $32\frac{1}{2}$ per cent. of lime could not be investigated, owing to the refractory nature of the oxides. The compounds formed are the metasilicate and the orthosilicate of calcium; the analogue, $4\text{CaO}, 3\text{SiO}_2$, of âkermanite, and the tricalcic silicate, $3\text{CaO}, \text{SiO}_2$, could not be detected, although special efforts were made to prepare them.

The properties of the metasilicate have been already described. The orthosilicate, $2\text{CaO}, \text{SiO}_2$, melts at about 2080° , and exists in three polymorphic forms which stand in enantiotropic relation to one another. The α -form, which crystallises in the monoclinic system, is the only modification stable in contact with the fusion. Its specific gravity is about 3.27. Below 1410° the α -form changes into the β -form. This unstable modification is orthorhombic, and has about the same density as the α -form; it turns into the monoclinic γ -variety at about 675° with great increase of volume, the specific gravity of the latter being 2.974. The disintegration which takes place when the orthosilicate is cooled is thus explained. The orthosilicate is readily attacked by water, and this is probably the reason why it is not found as a mineral. The three eutectics are: tridymite and pseudo-wollastonite at 37 per cent. of lime, melting at 1417° ; pseudo-wollastonite and α -orthosilicate at 54 per cent. of lime, melting at 1430° ; α -orthosilicate and lime at $67\frac{1}{2}$ per cent. of lime, melting at 2015° .

The preliminary investigation having demonstrated the existence of two compounds and three eutectics, the melting points of 100 gram charges were determined by means of a thermo-junction, or for higher temperatures by the Holborn-Kurlbaum pyrometer. The results, which were plotted, fully confirmed the preliminary observations. It was found incidentally that pseudo-wollastonite appears to be capable of taking up small quantities of silica and of orthosilicate in solid solution.

The very important results obtained in the course of the investigation of the feldspars and of the calcium silicates naturally led the workers in the geophysical laboratory at Washington to turn their attention to the compounds of magnesia and silica, and thanks to the labours of E. T. Allen, F. E. Wright, and J. K. Clement,¹ we now possess a very complete knowledge of the metasilicate, MgSiO_3 . This substance can exist in four distinct crystal forms.

I. The first crystallises in the monoclinic system, and is the product usually obtained from fusions. It was first prepared by Ebelmen, and

¹ *Amer. J. Sci.*, [iv], 22, 385.

is found in nature in certain meteorites. It can be made (1) by melting together magnesia and silica in the proper proportions and allowing the liquid to crystallise; (2) by allowing the glass obtained by rapidly cooling the fusion to crystallise at 1300° ; (3) by heating any of the other forms to temperatures from 1150° upwards; (4) by fusing amorphous silica with magnesium tellurite or chloride; (5) by recrystallising magnesium silicate from a flux of magnesium chloride or vanadate, calcium vanadate or tellurium dioxide. The first method is most suited for preparing the substance in quantity; the last yields the best crystals, the most satisfactory results being obtained when the silicate is fused with magnesium chloride in a current of dry hydrogen chloride. The crystals resemble in some respects those of a monoclinic pyroxene, having the characteristic cleavage angle 92° , but the ratio $b:c=0.77$ is very different from that of diopside $b:c=0.5894$. They are characterised by the low extinction angle on b (010), $c:r=21.8^{\circ}$, and by polysynthetic twinning parallel to a (100). The specific gravity is 3.192 at 25° . The monoclinic pyroxene met with in the Bishopville meteorite has the same properties.

II. The second form is orthorhombic and identical with enstatite. It is best prepared by heating the glass to between 1000° and 1100° ; if the latter temperature is exceeded the first variety appears as well, often in parallel intergrowths. Obtained in this way, the substance forms fibrous aggregates of specific gravity 3.175. The angle between the optic axes is smaller than that of natural enstatite, a fact as yet unexplained. On heating to temperatures above 1260° this form passes slowly into the monoclinic variety.

III. The third form is a monoclinic amphibole, and is the least clearly defined of the four. Its identification as a separate variety rests on its extinction angle, maximum value 11° , and on its mean refractive index, which is much lower than that of I. It is sometimes met with in fusions which have been rapidly cooled, and appears also to be produced by the action of water at $375-475^{\circ}$ on the next variety.

IV. This form is orthorhombic, and is identified by the authors with a naturally occurring amphibole to which some writers have given the name of kupfferite. To prepare this variety the mixture should be heated well above the melting point and then cooled as quickly as is possible without forming glass. Measurable crystals have not been obtained, and the identification with kupfferite rests on the optical properties and the indication of cleavage at 120° . The mean specific gravity is 2.857 at 25° . This variety changes into I on heating. These four modifications stand in monotropic relation to one another, the order of increasing stability being orthorhombic amphibole, monoclinic amphibole, enstatite, monoclinic pyroxene.

That this is so is shown by the fact that enstatite and the amphiboles when heated pass over into the monoclinic pyroxene, which cannot be changed back without passing through the amorphous state. Further, it is found that although the first three forms can all be dissolved in suitable fluxes at comparatively low temperatures, yet they crystallise out as monoclinic pyroxene. Lastly, it has been shown by an ingenious application of Frankenheim's method that the first three forms change into the monoclinic variety with evolution of heat. The existence of a monotropic relation between the two great groups of amphiboles and pyroxenes is in accord with the work of other experimenters, and the formation of amphiboles in nature instead of pyroxenes may perhaps have been due to the viscosity of the magma from which they crystallised, while the presence in the Bishopville meteorite of intergrowths of pyroxene and enstatite suggests that it was rapidly cooled from a high temperature.

Certain meta- and ortho-silicates have also been studied from a somewhat different point of view by V. Pöschl,¹ who has prepared mixed crystals by melting the constituents together. Thus he finds that artificial diopside and hedenbergite from Elba mix in all proportions. The melting point curve corresponds to Roozeboom's type I, but is not quite regular and the specific gravities of the mixtures do not in all cases lie between those of the components. Experiments with enstatite and diopside indicate that these substances form an isodimorphous series, with a gap extending from $40\text{CaMgSi}_2\text{O}_6$, $60\text{Mg}_2\text{Si}_2\text{O}_6$, to $50\text{CaMgSi}_2\text{O}_6$, $50\text{Mg}_2\text{Si}_2\text{O}_6$. The case is similar to that of the mixed sulphates of iron and magnesium, and the specific gravities are lower for the rhombic than for the monoclinic form. The melting point curve is of type V. Artificial mixtures of the isomorphous orthosilicates, Mg_2SiO_4 and Fe_2SiO_4 , do not give a continuous series, the gap extending from $65\text{Mg}_2\text{SiO}_4$, $35\text{Fe}_2\text{SiO}_4$ to $3\text{Mg}_2\text{SiO}_4$, $97\text{Fe}_2\text{SiO}_4$. The melting point curve is of type I, but is not a straight line. Artificial mixtures of Mg_2SiO_4 and Ca_2SiO_4 give results indicating that these substances are isodimorphous.

The conditions under which quartz and tridymite crystallise from silicate fusions have also been studied by P. D. Quensel,² who has arrived at conclusions in the main much the same as those reached by Day and Shepherd. He found that when a mixture of 74 parts of oligoclase and 26 parts of amorphous silica was fused with small quantities of tungstic oxide, or in the presence of water supplied by driving a current of superheated steam through the fusion, small quartz crystals were formed. The effect of adding tungstic oxide was to lower the melting point and

¹ *Centr. Min.*, 1906, 571.

² *Centr. Min.*, 1906, 657, 728; see also a paper by Cosmo Johns, *Geol. Mag.*, 1906, 3, 118.

viscosity, and to increase the size and rapidity of formation of the crystals. On fusing silica with excess of sodium tungstate, tridymite was obtained, a fact previously noticed by Hautefeuille. As there seemed reason to think that the amount of "mineraliser" present (in this case tungstic oxide or sodium tungstate) had an important influence on the result, fresh experiments were undertaken in which the oligoclase-silica mixture or pure silica were fused with from one to five parts of sodium tungstate. It was found, however, that quartz was always obtained from the oligoclase-silica mixture at temperatures below 1000° , while if silica alone was used, tridymite or glass were formed, according as the temperature was kept above or below 1000° , the amount of sodium tungstate present being unimportant. Quensel therefore concludes that the factors which determine the products are, the presence of co-solutes, the concentration, and the existence of chemical equilibrium, and explains the formation of quartz as due to the influence of the constituents of oligoclase on the equilibrium between the alkalis and silicic acid. In the case of tridymite a sodium silicate or possibly a silicotungstate is perhaps first formed, and this being unstable at high temperatures the silica separates directly as tridymite. The rare occurrence of tridymite in eruptive rocks, in spite of the fact that the temperature conditions would favour its formation, he explains as due to the special conditions required to produce this form, the presence of other substances interfering with its crystallisation.

Quensel finds that the melting point of tridymite is about 1560° , and concludes from his own work and from that of his predecessors that above 900° it is the stable form of silica. It can, however, exist at temperatures as low as 300° to 400° . Quartz, on the other hand, can exist up to 1000° , but is unstable above 900° . Below 200° the hydroxides are perhaps to be considered the stable form, though quartz can exist as well.

While the Americans have been breaking fresh ground in the study of pure silicates, C. Doelter has been very active in the field he has made especially his own. Many pages of the numerous and lengthy papers for which he and his pupils are responsible are occupied by adverse criticism of the views held by Vogt and of the results obtained by Day and Allen, but a certain amount of fresh work along the lines already familiar has been accomplished. Thus Doelter¹ himself has redetermined the melting points of a number of natural felspars, and has obtained results lower than those given by Day and Allen in their work on the artificial compounds. Further, he has reiterated his belief that when silicates are melted they dissociate to a very considerable extent into oxides, and has laid great stress on the part played by viscosity,

¹ *Wien. Sitzungsber.*, 1906, **115**, 723; *Monatsh.*, 1906, **27**, 433; *Tsch. Min. Mitt.*, 1906, **25**, 79 and 206; *Zeit. Elektrochem.*, 1906, **12**, 413; *Centr. Min.*, 1906, 193.

crystallising power, and velocity of crystallisation in determining the particular compounds which separate from a magma.

The relation between the composition of the mixture and that of the eutectic is regarded by him as of very minor importance. This point has been specially studied by M. Vučnik,¹ who has attempted to test Vogt's view in the case of certain binary mixtures, as for instance anorthite and fayalite, or anorthite and olivine. No eutectic structure was observed, but that mixture had the lowest melting point for which the composition was that required by theory for the eutectic. M. Vučnik and H. H. Reiter² have also examined the effect of fusing a number of ternary mixtures such as anorthite, hedenbergite, and olivine; leucite, olivine, and aegirine; labradorite, aegirine, and elalite; albite, augite, and magnetite, &c. As can readily be imagined, the results obtained are complex, and substances like spinel and hematite not present in the original mixture crystallise out on cooling. Such facts as these they regard as evidence that dissociation of the original silicates has taken place. The general conclusion drawn from the experiments is that from fusions of this kind minerals separate in the following order: spinel, hematite, magnetite, olivine, magnetite (2), augite, magnetite (3), nepheline, plagioclase. This order is conditioned by the chemical reactions accompanying the dissociation of the silicates, as well as by the composition of the mixture and its relation to that of the eutectic. That supersaturation may play an important part is to be gathered from the fact that magnetite can appear at more than one stage, while viscosity, velocity of cooling, and power of crystallisation all have a share in determining the result. They find in these experiments no confirmation of Vogt's views as to the importance of the eutectic in determining the order of crystallisation.

J. H. L. Vogt himself, on the other hand, continues to insist most vigorously that the laws of physical chemistry established by the study of solutions are directly applicable to mixtures of molten silicates, which he regards as but slightly, if at all, dissociated. He has recently contributed a masterly exposition of his views to the pages of *Tschermak's Mineralogische Mitteilungen*.³ This begins with a brief *résumé* of the laws governing the solidification of binary and ternary mixtures, and includes an account of Roozeboom's classification of mixed crystals. The application of these principles to slags is next discussed, and van't Hoff's law of molecular freezing point depression shown to hold for such cases as åkermanite and augite, melilite and anorthite, diopside and olivine, melilite and olivine. Incidentally the conviction is expressed that Doelter's experiments in this direction are not calculated to throw much light on the subject.

¹ *Centr. Min.*, 1906, 132.

² *Jahrb. Min.* 1906, *Beil. Bd.*, 22, 182.

³ 1906, 24, 437—542.

In a succeeding paragraph the mixed crystals formed by Mg_2SiO_4 and Fe_2SiO_4 are shown to belong to type I of Roozeboom's classification, and the importance of zonal structure as indicating a slight degree of supersaturation is pointed out. Arguments are also adduced to show that the mixed crystals formed by enstatite and diopside fall under Roozeboom's type IV. The results obtained by Day and Allen are utilised in the elaborate discussion of the feldspars which occupies the second half of Vogt's paper and is devoted mainly to the consideration of mixed crystals composed of orthoclase, albite, and anorthite. It is shown that whereas the binary mixture, albite and anorthite, belong to type I, the mixtures of orthoclase with albite or anorthite belong to type V and form eutectics. The ternary mixture in which all three components are present is also discussed and illustrated by a diagram. Further, the work of Schreinemakers¹ is applied to the case in which the mixture of orthoclase and albite is present with some independent component such as quartz or olivine. Such a case must fall either under Schreinemakers' type *d* or type *e*, and it is stated that the combination quartz, orthoclase, albite belongs to the second of these, and yields as final product a ternary eutectic mixture of quartz and the two kinds of mixed crystals. A full discussion of some of the latter points is to be given in a continuation of the paper.

Deposition of Quartz from Aqueous Solutions.—J. G. Königsberger and W. J. Müller² have attempted to throw light on the conditions under which quartz and other vein minerals have been deposited, more especially in the case of those found in the biotite-protogine of the Aar. Assuming that these minerals have crystallised from solutions having approximately the composition of the inclusions found in the quartz crystals of the district (see page 323) at temperatures between 120° and 500°, they have attempted to imitate the conditions of their formation by heating glass and obsidian with water and carbon dioxide in a steel bomb lined with platinum-iridium. The bomb was heated in an electrical oven in which it could be shaken and inverted. On inversion a filtering arrangement came into action which enabled them to examine separately the crystals deposited from the solution on cooling.

The composition of the glass (I) and obsidian (II) was :—

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	MgO .	CaO .	K_2O .	Na_2O .	H_2O .
I.	69.21	2.48	0.45	0.52	9.84	1.98	14.91	—
II.	74.3	13.0	2.6	0.3	1.00	4.6	3.8	0.3

The glass was completely decomposed on heating with water to 360°, and quartz crystals and some opal were found to have separated from the solution. The residue in the tube consisted chiefly of amorphous

¹ *Zeit. physikal. Chem.*, 1905, **51**, 569.

² *Centr. Min.*, 1906, 339, 353.

silica, together with tridymite and a little quartz. The glass was also decomposed if the water contained small quantities of carbon dioxide, but if much was present the glass was less readily attacked. Obsidian treated with water was more resistant than glass, but on adding sodium bicarbonate decomposition took place and quartz was formed. When heated to 420° with a solution of the composition of the quartz inclusions, obsidian was partially converted into a substance identified with aegirine-augite. Zeolites were not observed in these experiments. Quartz, muscovite, and adularia were all more or less attacked by water at 350° , and dissolved completely when heated to the same temperature with a 20 per cent. solution of sodium carbonate, carbon dioxide escaping from the tube, which was not quite tight. On the other hand, water containing both carbon dioxide and sodium carbonate had very little action on quartz, adularia, sphene, muscovite, biotite, calcite, or fluorite at 370° . The action of alkali carbonates first becomes considerable at those temperatures at which they are strongly hydrolysed. The addition of carbonic acid diminishes the hydrolysis, and in consequence the action of the alkali. This is in harmony with the experiments of Spezia, who found that the action of a solution of borax on quartz was diminished by the addition of boric acid. The most important conclusion arrived at by the authors is that in the system composed of silicic acid, alkalis, and a weak acid such as carbonic acid or boric acid in aqueous solution, the deposition of quartz can only be explained by a change in the equilibrium point of a reversible reaction, the acidity of the silicic acid increasing with greater rapidity as the temperature rises than it does in the case of the other weak acid present. They also point out that the simultaneous production of quartz, tridymite, opal, and chalcedony is in harmony with van't Hoff's rule that high valence favours the existence of labile compounds.

The Silicic Acids.—G. Tschermak¹ and his pupils have carried out a good deal of new work on the lines described last year, and believe that they have established the existence of several new silicic acids, and thereby thrown light on the constitution of a number of minerals. Ilvaite, anorthite, and olivine all yield metasilicic acid, H_2SiO_3 , and must therefore be regarded as metasilicates. Willemite and monticellite are orthosilicates. Pectolite and wollastonite both yield $\text{H}_6\text{Si}_3\text{O}_9$, and wollastonite is therefore $\text{Ca}_3\text{Si}_3\text{O}_9$. Meerschaum from Asia Minor also gave an acid, $\text{H}_6\text{Si}_3\text{O}_9$. Massive and foliated serpentine and also chrysotile were found to have the composition $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$, but whilst the latter gave an acid, $\text{H}_{10}\text{Si}_4\text{O}_{13}$, the former

¹ *Wien. Sitzungsber.*, 1906, **115**, i, 217, 697; *Anzeiger K. Akad. Wiss. Wien.*, 1906, **19**, 339.

gave $\text{H}_8\text{Si}_4\text{O}_{12}$, and the same substance was obtained from the pseudomorphs of serpentine after olivine from Snarum. Chrysotile is therefore to be written $\text{H}_4(\text{MgOH})_4(\text{MgOMg})\text{Si}_4\text{O}_{13}$, and serpentine $\text{H}_2(\text{MgOH})_6\text{Si}_4\text{O}_{12}$. From datolite and gadolinite a new pulverulent acid, $\text{H}_2\text{Si}_2\text{O}_5$, was obtained. Heulandite, taken to be $\text{H}_{12}\text{CaAl}_2\text{Si}_6\text{O}_{22}$, gave an acid, $\text{H}_{10}\text{Si}_6\text{O}_{17}$, and must be written $\text{H}_8(\text{CaO}_2\text{Al}_2\text{O}_2\text{H}_2)\text{Si}_6\text{O}_{17}, \text{H}_2\text{O}$, the bivalent group HOAlOCaOAlOH being present. They find, moreover, that heulandite lost calcium when exposed to the action of a considerable quantity of water, and therefore conclude that it was probably deposited from a concentrated solution.

Constitution of Zeolites.—Reference was made last year¹ to the experiments of F. Zambonini on heulandite and on thomsonite, by which he attempted to throw light on the vexed question of the part played by water in these compounds. The conclusion to which he then came was that these minerals are comparable to the hydrogels described by van Bemmelen. He has been confirmed in this view by his recent researches,² which have been conducted on lines similar to those already described. Thus he finds that the dehydration of, and the reabsorption of water by, gelatinous silica prepared from potassium silicate follows much the same course as in the case of the zeolites. The amorphous nickel ore garnierite, $(\text{Mg}, \text{Ni})\text{SiO}_3, n\text{H}_2\text{O}$, from Noumea, New Caledonia, on the other hand, exhibits a very different behaviour from heulandite and thomsonite as regards its capacity for reabsorbing water after partial dehydration at various temperatures. This substance is probably a solid solution, and it is therefore hardly likely that the zeolites are to be regarded as having the same constitution. Further, he concludes that the water taken up again by zeolites after they have been heated is more loosely held than the water originally present, and he bases this statement on the dehydration curves of the rehydrated zeolite. Lastly, observations made on diopside lead him to the somewhat remarkable conclusion that in the case of this mineral we meet with an example of solid solution.

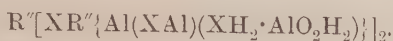
The constitution of certain silicates has also been discussed by H. C. McNeil,³ who, continuing the line of research begun by F. W. Clarke, has examined the behaviour of various minerals when treated with strong solutions of hydrochloric acid and sodium carbonate both before and after ignition. He finds that talc which has been strongly heated contains one-fourth of its silica in a form soluble in sodium carbonate, the residue being completely decomposed by hydrochloric acid. He concludes that talc contains both an ortho- and a tri-silicate radicle, and that the latter on ignition turns into an Si_2O_5 group. Pyrophyllite he regards as a true acid metasilicate.

¹ *Ann. Report*, 1905, 271.

² *Mem. R. Accad. Lincei*, 1906, 6, 102.

³ *J. Amer. Chem. Soc.*, 1906, 28, 590.

The results obtained with kaolin accord with the supposition that it is an orthosilicate, $\text{HOAl}(\text{OSiO}_3\text{H}_3)(\text{OSiO}_3\text{Al})$, converted, on heating, into $\text{Al}_2\text{Si}_2\text{O}_7$ and water. Halloysite on ignition also gives $\text{Al}_2\text{Si}_2\text{O}_7$, and may be regarded as kaolin combined with one molecule of water. McNeil has also carried out some experiments on zeolites, on the lines of those made by Steiger, but instead of using sealed tubes he has fused the minerals with various chlorides in platinum crucibles. As the result of experiments in which chabazite, stilbite, and thomsonite were fused with sodium chloride, he believes that these silicates belong to the same class and have the following general formula:



In thomsonite X is chiefly SiO_4 in stilbite Si_3O_8 , and in chabazite a mixture of both these groups.

Mutual Relations of Fused Chlorides.—Some fresh light has been thrown on the minerals of the cerargyrite family by the work of K. Mönkemeyer,¹ who has studied the freezing point curves of binary mixtures of AgCl , AgBr , and AgI . These three substances melt at 452° , 422° , and 552° respectively. The two former crystallise in the holohedral class of the cubic system, but the iodide is dimorphous, the cubic form being stable above $146\frac{1}{2}^\circ$, whilst below that temperature the substance forms hexagonal crystals. In the case of the mixture AgCl - AgBr , the freezing point curve is of type III of Roozeboom's classification. A continuous series of mixed crystals of the same kind is formed, and a minimum freezing point lying below the melting point of the more fusible constituent is reached. The minimum 412° was found to correspond to the mixture containing 35 per cent. of silver chloride. The mixtures of bromide and iodide also conform to type III, the minimum value of the freezing point being 377° , corresponding to the mixture containing 73 per cent. of silver bromide. In this case the phenomena are further complicated by the transformation of cubic into hexagonal crystals conditioned by the presence of the iodide. This transformation falls under type IA of Roozeboom's scheme, the mixed crystals forming a continuous series before and after the change, only one component being dimorphous. In the case of the chloride and iodide mixture the freezing point curve is of type V. The series of mixed crystals is interrupted, and a eutectic occurs containing 42 per cent. of silver chloride and solidifying at 211° . The chloride is only capable of taking up very small quantities of iodide, while the latter will mix with as much as 13 per cent. of chloride. The transformation into hexagonal crystals conforms to type IIIA. The view suggested by L. J. Spencer's study of miersite, that silver iodide

¹ *Jahrb. Min. 1906, Beil.-Bd., 22, 1.*

is trimorphous, has not received any confirmation from these experiments.

Water of Crystallisation.—The difficult question as to the manner in which the elements of water are combined in minerals has been attacked by W. W. Coblentz¹ in an ingenious way. The infra-red absorption spectrum of water exhibits well-marked bands at the approximate wave-lengths 1·5, 2, 3, 4·75, and 6 μ , those at 3 and at 6 being especially strong. Coblentz has therefore examined a large number of minerals to see if those containing so-called "water of crystallisation" show the water bands. In the case of selenite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, he found that these bands were strongly marked, with the exception of that at 4·75, the place of which was taken by a strong band at 4·55. Anhydrite, CaSO_4 , on the other hand, did not show the water bands, although in this case also the band at 4·55 was prominent. This band was subsequently found to be well shown by anglesite, barytes, and celestine, as well as by glauberite, kieserite, and thenardite; it is doubtless due to the SO_4 ion. Opal, heulandite, stilbite, natrolite, and scolecite all showed the water bands. On examining hydroxides the water bands were found to be wanting, with the exception of that at 3, which appears to be characteristic of this class of substances. This was found to hold for manganite, göthite, bauxite, turquoise, lazulite, hydrargyllite, and diaspore. In the case of datolite and azurite the band at 3 was slightly displaced, while brucite exhibited a complex band with maxima at 2·5, 2·7, and 3. Tourmaline showed bands at 1·28 and 2·82. The examination of chloritoid, clinocllore, pennine, the micas, and talc revealed no indication of the presence of hydroxyl. On the other hand, this group probably exists in serpentine, which shows a well-marked band at 3 μ .

New Minerals.

Bellite.—This mineral has been described by W. F. Petterd.² It occurs in delicate tufts and velvety coatings lining cavities in a soft iron-manganese-gossan at Magnet silver mine, Magnet, Tasmania. Minute hexagonal scales are sometimes met with. The colour is bright crimson to orange-yellow. Sp. gr. 5·5.

The following analysis is by J. D. Millen :

SiO_2 .	PbO .	CrO_3 .	SO_3 .	As_2O_5 .	P_2O_5 .	V_2O_5 .	Al_2O_3 .	Cl.	Total.
7·59	61·68	22·61	0·05	6·55	0·04	0·11	0·01	0·52	99·16

Chlormanganokalite.—A preliminary account of this mineral has been given by H. J. Johnston-Lavis,³ who found it in the form of canary-yellow rhombohedra associated with halite inside a block ejected

¹ *Physical Review*, 1906, **23**, 125.

² *Tasmania. Report of Secretary for Mines for 1904. Hobart*, 1905, 83.

³ *Nature*, 1906, **74**, 103. See also A. Lacroix, *Compt. rend.*, 1906, **142**, 1249.

from Vesuvius. Analysis shows that the mineral is essentially a double chloride of manganese and potassium containing 38·97 per cent. of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 57·71 per cent. of KCl .

Chlornatrokalite.—This name has been given by Johnston-Lavis¹ to a *sylvite* containing 12 per cent. of NaCl , found associated with chlormanganokalite.

Gorceixite is a barium aluminium phosphate. It occurs in brown pebbles, so-called “favas,” in the diamond sands of Brazil, and has been described by E. Hussak.² Omitting silica (present as included quartz grains), ferric oxide, and TiO_2 , the two following analyses by G. Florence lead to the formula $\text{BaO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, a portion of the barium being replaced by calcium and cerium, and occasionally by strontium :

	$\cdot\text{SiO}_2$	TiO_2	BaO	CaO	CeO	Al_2O_3	Fe_2O_3	P_2O_5	H_2O
I.	1·55	0·67	15·42	3·55	1·55	35·00	4·10	22·74	14·62
II.	6·5	0·75	15·30	2·24	2·35	35·20	1·67	21·47	14·73

Harttite.—E. Hussak³ has assigned this name to a strontium aluminium sulphato-phosphate found in flesh-coloured “favas” in the diamond sands of Brazil. The mineral is related to *svanbergite*, $2\text{SrO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 2\text{SO}_3 \cdot 6\text{H}_2\text{O}$, and has been analysed by G. Florence, with the following results :

TiO_2	Al_2O_3	SrO	CaO	CeO	P_2O_5	SO_3	H_2O
1·42	33·66	16·80	2·80	1·02	21·17	11·53	12·53

These numbers lead to the formula $(\text{Sr}, \text{Ca})\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$.

Hydrated Calcium Carbonate.—A deposit from the neighbourhood of Novo-Alexandria, looking much like mould or a thin layer of cotton-wool, has been examined by L. L. Ivanoff,⁴ who finds that it consists of very thin, colourless, transparent, monoclinic or triclinic needles. When kept over calcium chloride at 22° , it loses 37·56 per cent. of water, leaving practically pure calcium carbonate behind. It is to be regarded as a hydrate, $\text{CaCO}_3 \cdot n\text{H}_2\text{O}$, where n is not less than 3.

Kertschenite.—At one or two localities in the Kertsch Peninsula there is found a dark green or almost black mineral. The formula $(\text{Fe}, \text{Mn}, \text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ has been given to it by S. P. Popoff⁵ on the ground of the two following analyses :

P_2O_5	Fe_2O_3	FeO	MnO	MgO	CaO	H_2O	Total.
28·19	32·89	9·50	1·99	1·54	0·49	25·04	99·64
28·21	32·965	9·49	1·84	1·56	0·46	24·91	99·435

New Mercury Mineral.—In 1903 A. J. Moses described two new mineral species, eglestonite and terlinguaite, both oxychlorides of mercury, from the Terlingua district, Texas, and indicated the probable existence of a third. The last is now under investigation by W. F.

¹ *Nature*, 1906, **74**, 174.

² *Tsch. Min. Mitt.*, 1906, **25**, 335.

³ *Ibid.*, 335.

⁴ *Ann. Geol. Min. Russie*, 1905, **8**, 23.

⁵ *Centr. Min.* 1906, 112.

Hillebrand and W. T. Schaller.¹ The preliminary examination has rendered it almost certain that this remarkable substance is a mercur-ammonium salt. It has so far been shown to contain Hg, N, Cl, SO₄, probably O, and possibly H. Further, P. G. Nutting has found that it gives off a little helium on warming. The full account of this as yet unnamed mineral will be awaited with interest. In the meantime we may note that A. Sachs² has suggested that the oxychloride of mercury, 3HgO, HgCl₂, described by him last year under the name of kleinite, may be identical with the substance referred to by Hillebrand. He finds, in fact, that both the sulphur-yellow and the orange-red varieties of kleinite yield small and variable amounts of SO₄ and ammonia, and he suggests that a portion of the chlorine in the above formula is perhaps replaced by SO₄, whilst oxygen is substituted by NH₂. If these views are accepted, the formula of kleinite becomes Hg₄[Cl_{1/2}SO₄]₂[O(NH₂)₂]₃.

Moravite.—Under this name F. Kretschmer³ has described a new member of the leptochlorite family, found in considerable quantity in the neighbourhood of Gobitschau, near Sternberg, Moravia. It occurs in scales and lamellæ, iron-black in colour, and in physical characters and mode of occurrence it somewhat resembles thuringite, from which it may be distinguished by its superior hardness and lower specific gravity, as well as by its different composition. The results obtained on analysis of two different carefully selected specimens were as follows :

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O + Na ₂ O.	P ₂ O ₅ .	C.	H ₂ O.
I.	49·30	22·71	5·04	13·99	trace	1·82	1·10	trace	0·55	4·95
II.	50·69	19·62	10·42	8·30	0·84	1·46	(?)	0·93	(?)	5·02

From I is derived the formula H₄(Al, Fe)₄(Fe, Mg)₂Si₇O₂₄. The other members of the group found at Gobitschau are :

Thuringite, H₁₈(Al, Fe)₈(Fe, Mg)₈Si₆O₄₁.

Stilpnochlorane, H₂₄(Al, Fe)₁₀(Ca, Mg)Si₉O₄₆.

Stilpnomelane, H₁₂(Al, Fe)₂(Fe, Mg)₈Si₁₀O₃₇.

Nepouite.—Under this name E. Glasser⁴ has recently described a mineral somewhat resembling Breithaupt's connarite. It occurs in the form of a crystalline powder at Népoui, New Caledonia. Five different specimens have been analysed, and the results quoted below are in harmony with the formula 2SiO₂·3(Ni, Mg)O·2H₂O, nickel and magnesium being mutually replaceable in all proportions :

	SiO ₂ .	NiO.	MgO.	FeO.	CaO.	Al ₂ O ₃ .	H ₂ O.	Total.	Sp. gr.
I.	32·84	49·05	3·64	1·90	0·50	0·97	9·64	98·54	3·24
II.	33·03	46·11	6·47	2·20	traces	1·39	10·61	99·81	3·18
III.	35·05	39·99	11·80	1·22	0·58	1·13	10·05	99·82	2·89
IV.	40·07	18·21	29·84	0·25	0·53	0·72	11·98	101·60	2·47
V.	32·36	50·70	3·00	0·62	traces	0·69	12·31	99·68	3·20

¹ *Amer. J. Sci.*, 1906, [iv], 21, 85.

³ *Ibid.*, 293.

² *Centr. Min.*, 1906, 200.

⁴ *Compt. rend.*, 1906, 143, 1173.

Oehlrite.—The formula $6\text{SiO}_2, 6(\text{Mg} + \text{Fe}, \text{Ca})\text{O}, \text{H}_2\text{O}$ has been given by E. S. Fedoroff¹ to a mineral of the following composition :

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MgO .	CaO .	Na_2O .	K_2O .	H_2O .
49.47	6.74	0.23	6.33	16.80	17.74	0.38	0.18	2.41

It occurs in the Jenashir district of the Caucasus and somewhat resembles diallage in appearance. It has three rectangular cleavages, (100), (010), (001), the latter being highly perfect, but crystallises in the monoclinic system as shown by the optical characters. The optic axes lie in the plane of symmetry, the acute positive bisectrix making an angle of 55° with the normal to (001). The angle $2V$ is 63° .

Osannite is a variety of amphibole, intermediate between riebeckite and arfvedsonite, and is found in the gneissic rocks of Cevadaes, Portugal. The optical characters have been determined by C. Hlawatsch,² who points out that in the amphiboles these properties vary with the ratio $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$, and also possibly with the amount of water present. The following analysis is due to M. Dittrich :

SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .	CaO .	Na_2O .	K_2O .	H_2O .	Total.
49.55	0.34	0.97	16.52	20.38	1.30	0.16	0.90	6.53	0.85	1.85	99.35

Otavite is a basic cadmium carbonate containing 61.5 per cent. of cadmium, found by O. Schneider³ as white to reddish crusts lining cavities on two specimens from the Tschumeb mine, Otavi, German South-West Africa. The crusts consist of minute rhombohedra ($rr' = 80^\circ$ about), which dissolve with effervescence in hydrochloric acid, and exhibit a metallic to adamantine lustre.

Paratacamite.—G. F. Herbert Smith⁴ has proposed this name for a mineral of the same composition as atacamite, $\text{CuCl}_2, 3\text{Cu}(\text{OH})_2$, which he has observed on some specimens from Chili. The crystals are of two habits, namely, rhombohedral and prismatic. They are frequently twinned, and have a good cleavage parallel to the rhombohedron faces. The specific gravity is 3.74. The refractive index, 1.846. On heating the mineral it appears to give up its water rather more readily than does atacamite. According to G. T. Prior, the composition is :

CuO .	Cu .	Cl .	H_2O .
56.10	14.27	15.97	14.10

Paravivianite.—Radiating needle-like crystals, transparent and somewhat blue in colour, occur in the limonite ore of the Kertsch Peninsula. The formula $(\text{Fe}, \text{Mn}, \text{Mg})_3\text{P}_2\text{O}_8, 8\text{H}_2\text{O}$ has been found by

¹ *Gorni Journal*, 1905, 264.

² *Festschrift Harry Rosenbusch*, Stuttgart, 1906, 68.

³ *Centr. Min.*, 1906, 389.

⁴ *Min. Mag.*, 1906, 14, 170.

S. P. Popoff¹ to agree well with the analytical results. No ferric iron is present.

P ₂ O ₅ .	FeO.	MnO.	MgO.	CaO.	H ₂ O.	Sp. gr.
27·01	39·12	2·01	1·92	0·48	29·41	2·66

Patronite.—Under this name F. Hewett² has recently described a dark green substance containing vanadium, which appears to occur in some quantity at Cerro de Pasco, Peru. A specimen of the crude ore was found to contain 16 per cent. of vanadium and 54 per cent. of sulphur, with considerable quantities of silica, alumina, and iron. It is at present undergoing examination at the hands of Dr. Hillebrand.

Rutherfordine.—This interesting mineral occurs associated with mica in German East Africa, and is an alteration product of pitchblende. The following analysis by W. Marekwald³ shows that it is uranyl carbonate, UO₂CO₃. In appearance it resembles uranochre.

UO ₃ .	CO ₂ .	PbO.	FeO.	CaO.	H ₂ O.	Gangue.	Total.	Sp. gr.
83·8	12·1	1·0	0·8	1·1	0·7	0·8	100·3	4·82

Silicomagnesiofluorite.—This curious mineral has been found as a loose block composed of radiating hemispherical aggregates, grey or green in colour, at Luppiko, in the neighbourhood of Pitkäranta, Finland. It has been examined by P. A. Zemjatschensky,⁴ who assigns to it the formula H₂Ca₄Mg₃Si₂O₇F₁₀, which he thinks may also be written in the form Mg(OH)F, MgSiO₃, Ca(OH)F, CaSiO₂F₂, 2CaF₂, MgF₂. The fibres show straight extinction and weak positive double refraction. The specific gravity is 2·9125 at 20°.

Weinbergerite.—In the course of an examination of the Kodaikanal meteorite, F. Berwerth⁵ has found a new silicate in the form of spherules exhibiting fibrous structure, associated with diopside, bronzite, apatite, and chromite. It appears to crystallise in the orthorhombic system, and its refraction and double refraction are both very low. There is reason to believe that it is pseudomorphous. According to E. Ludwig, the composition is :

SiO ₂ .	TiO ₂ .	P ₂ O ₅ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	MnO.	CaO.	MgO.
42·0	0·70	0·88	28·75	9·42	0·98	trace	3·87	4·47
		K ₂ O.	Na ₂ O.	H ₂ O.	Total.			
		2·57	3·19	2·17	99·0			

If we assume that the iron was present as FeO, that the water is not essential, and that P₂O₅ and Cr₂O₃ are due to the presence of apatite and chromite respectively, it will be found that the composition can be represented by the formula NaAlSiO₄ + 3FeSiO₃, some of the

¹ *Centr. Min.*, 1906, 112.

³ *Centr. Min.*, 1906, 761.

² *Engin. Mining Jour.*, 1906, 82, 385.

⁴ *Zeit. Kryst. Min.*, 1906, 42, 209.

⁵ *Tsch. Min. Mitt.*, 1906, 25, 179.

sodium being replaced by potassium, and some of the iron by magnesium and calcium.

Yttrocalcite.—A mineral described under this name by E. S. Fedoroff¹ in 1905 has proved on further investigation to be identical with fluorapatite.²

Yttrocrasite.—This name has been assigned by W. E. Hidden and C. H. Warren³ to an yttrium-thorium-uranium titanite. The material for analysis was derived from a single crystal weighing some sixty grams, found about three years ago in Burnet County, Texas, where the mineral occurs in loose pegmatite. The crystal exhibited orthorhombic symmetry and resembled certain yttrotantalites.

It was covered with a thin brown coating, the underlying material being black with pitchy lustre. Optical examination of thin slices showed that it was not strictly homogeneous, but consisted of isotropic and of feebly doubly refracting portions. Sp. gr. 4·8043 at 17°. The following are the results of Warren's analysis:

TiO ₂ .	WO ₃ .	UO ₃ .	CO ₂ .	(Yt,Er) ₂ O ₃ .	Ce ₂ O ₃ , &c.	Fe ₂ O ₃ .	ThO ₂ .	UO ₂ .
49·72	1·87	0·64	0·68	25·67	2·92	1·44	8·75	1·98
		PbO.	MnO.	CaO.	H ₂ O.	Total.		
		0·48	0·13	1·83	4·46	100·57		

A small quantity of Cb₂O₅ together with traces of Ta₂O₅, SiO₂, and MgO, were also found, and of the water 0·10 per cent. was hygroscopic. These numbers give the following approximate molecular ratios: H₂O : R''O : R'''₂O₃ : R''''O₂ : TiO₂ = 6 : 1 : 3 : 1 : 16, where R''O is chiefly lime, R''₂O₃ chiefly yttrium earths, and R''''O₂ chiefly thoria. The mineral is therefore essentially a hydrous titanate of the yttrium earths and thorium, but the fact that it contains both water and carbon dioxide, taken in conjunction with the results of the microscopic examination, suggests that it may be a hydrated alteration product of an originally anhydrous species. The radioactivity of the substance has been determined by B. B. Boltwood, who finds that it corresponds to 10 per cent. of thorium and 2·08 per cent. of uranium.

A New Zeolite.—A. Pauly⁴ has examined the minute grains scattered through a quartz-sericite rock which occurs in the neighbourhood of Hainburg. He finds that they are isotropic and possess a good cleavage parallel to faces of the cube. The index of refraction is 1·507—1·508 for sodium light, and is therefore higher than that of analcime. Microchemical tests showed the presence of Na, Ca, Si, Al, and SO₄. About 10 per cent. of water was driven off on heating, proving that the mineral is not a member of the sodalite group. The specific gravity is 2·4—2·5. The author has been unable so far to obtain

¹ *Gorni Journal*, 1905, 264.

² *Private communication* from E. S. Fedoroff.

³ *Amer. J. Sci.*, 1906, [iv], 22, 515.

⁴ *Zeit. Kryst. Min.*, 1906, 42, 370.

sufficient material for a quantitative analysis, but thinks that his results justify him in concluding that the mineral is new.

Artificial Formation of Minerals.

A number of cases of the artificial production of minerals have been mentioned incidentally in a previous section, but a few special experiments deserve a separate description here.

Diamond.—A useful summary of the attempts that have been made to obtain this form of carbon has been contributed by A. Koenig¹ to the pages of the *Zeitschrift für Elektrochemie*.

Forsterite.—Allen and Wright² obtained Mg_2SiO_4 as a by-product when MgSiO_3 was dissolved in fluxes and allowed to crystallise. The best specimens were furnished by magnesium chloride. The crystals were small, but gave fairly sharp measurements, and agreed in habit, angles, and physical characters with the natural mineral. *Periclase* was also observed in some of these experiments in well-formed octahedra.

Nordenskiöldite.—Minute but measurable rhombohedra of this substance, $\text{CaO}, \text{SnO}_2, \text{B}_2\text{O}_3$, have been obtained by L. Ouvrard³ by passing a mixture of air and stannic chloride vapour over calcium borate at a bright red heat.

Northupite, $2\text{MgCO}_3, 2\text{Na}_2\text{CO}_3, 2\text{NaCl}$, is probably isomorphous with tychite, $2\text{MgCO}_3, 2\text{Na}_2\text{CO}_3, \text{Na}_2\text{SO}_4$, described by Penfield and Jamieson last year. To throw light on this point, A. de Schulten⁴ has attempted to prepare mixed crystals of the two substances. In this he has been successful, for by heating mixtures of the chloride and sulphate of sodium in various proportions with 20 grams Na_2CO_3 and 18 grams $\text{Mg}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, dissolved in 350° c.c. of water, he has obtained crystals containing 99, 76, 64, 28, and 6 per cent. of tychite respectively. He concludes, therefore, that the two substances are perfectly isomorphous.

Quartz has been produced in measurable crystals by Day and Shepherd⁵ by heating a mixture of ammonium magnesium chloride, sodium metasilicate, and water for three days in a steel bomb at 400—450°. The clear, colourless crystals attained a maximum length of 2 mm. They were doubly terminated and often barrel-shaped, showing rhombohedron faces passing by oscillatory developments into steeper rhombohedra, and finally into the prisms which showed the characteristic striæ. In some the + rhombohedron only was present. The angle from prism to rhombohedron was 37°48' instead of

¹ *Zeit. Elektrochem.*, 1906, **12**, 441.

² *Amer. J. Sci.*, 1906, [iv], **22**, 390.

³ *Compt. rend.*, 1906, **143**, 315.

⁴ *Ibid.*, 403.

⁵ *Amer. J. Sci.*, 1906, [iv], **22**, 297.

38°13', this being perhaps due to some ingredient of the mixture held in solid solution.

Some interesting experiments on the crystallisation of quartz have also been carried out by G. Spezia.¹ He suspended a long crystal and three short prisms of quartz cut perpendicular to the axis in the lower portion of a tube containing a 2 per cent. solution of sodium metasilicate which was kept at a temperature of about 330° at the upper end, whilst the lower end remained at about 170°. The upper part of the solution was in contact with a quantity of powdered quartz. After heating for one hundred days, it was found that a quantity of silica had dissolved and had been deposited again on the prisms, converting them into more or less perfect crystals. The long crystal had also increased in size. It was observed that quick crystallisation appeared to favour the development of a long prism terminated by the faces of one rhombohedron. Slow crystallisation, on the other hand, gave a short prism terminated by the faces of two rhombohedra.

Mineral Analyses.

Many mineral analyses have been published during the past year. It is only possible here to refer very briefly to some of those which have thrown light on the composition of rare or imperfectly described species, or which are of special importance, because made on carefully selected material of which the crystallographic and physical characters have also been determined. For the rest, reference should be made to the Abstracts published by this Society.

Apatite.—Crystals from the Rhone glacier have been the subject of an elaborate crystallographic and optical study by K. Busz.² He finds $a : c = 1 : 0.7335$, and that for sodium light, $\omega = 1.63558$, $\epsilon = 1.63320$. A second prism gave slightly different values. The analysis quoted below shows that the substance is a pure fluor-apatite.

P ₂ O ₅ .	Al ₂ O ₃ .	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	F.	Sp. gr.
41.44	0.94	0.39	54.80	0.14	0.45	0.53	0.22	2.93	3.195

Traces of iron and chlorine were found.

Apophyllite.—In a preliminary communication F. Cornu³ announces that the extreme members of the leucocyclite type of apophyllite are free from fluorine, but contain hydroxyl; the specimens of the chromocyclite type, on the other hand, contain fluorine. The former are optically positive and possess higher indices of refraction than the latter, which are negative.

Berthierite.—This mineral occurs in some quantity at Charbes, Val

¹ *Atti R. Accad. Sci. Torino*, 1906, **41**, 158.

² *Centr. Min.*, 1906, 753.

³ *Ibid.*, 79.

de Villé (Weilerthal), Alsace. A specimen analysed by Ungemach¹ gave the following results :

S.	Sb.	Fe.	As.	SiO ₂ .	Total.	Sp. gr.
28·02	54·06	12·72	traces	5·29	100·09	4·21-4·23

On subtracting the silica, numbers are obtained which agree well with the formula $\text{FeS, Sb}_2\text{S}_3$.

Boleite Group.—G. Friedel² has published a comprehensive account of this group, based on an examination of specimens preserved at the École des Mines de Saint-Étienne, supplemented by some from the École des Mines de Paris. He has also been able to study Mallard's microscopic sections and some of Lacroix's preparations. He recognises three distinct species in the group, namely, cumengeite, pseudo-bolélite, and bolélite. All three crystallise in the tetragonal system, and their chief properties are summarised below :

Name.	Formula.	Parameter <i>c</i> .	Sp. gr.	Birefringence.
Cumengeite	$4\text{PbCl}_2, 4\text{CuO}, 5\text{H}_2\text{O}$	1·625	4·67	0·100
Pseudo-bolélite ...	$5\text{PbCl}_2, 4\text{CuO}, 6\text{H}_2\text{O}$	2·023	4·85	0·032
Boleite	$9\text{PbCl}_2, 8\text{CuO}, 3\text{AgCl}, 9\text{H}_2\text{O}$...	3·996	5·054	0·020

The above formulæ differ considerably from those hitherto assigned to members of the group, and are based on the following analyses, of which I refers to cumengeite, II to pseudo-bolélite, III gives the composition of pseudo-bolélite on the assumption that the silver chloride present is due to admixture with boleite ; IV is the mean of two concordant analyses of boleite made, one on material derived from the exterior of the crystals, the other on material from the interior. Under Ia, IIIa, and IVa are given the theoretical percentages corresponding with the formulæ. As the analysis of pseudo-bolélite was made on 0·0948 gram only, and as the water yielded by this substance could only be obtained by calculation from an estimation made on a mixture of boleite and pseudo-bolélite, of which the composition was but approximately known, the formula assigned can only be regarded as provisional.

	I.	Ia.	II.	III.	IIIa.	IV.	IVa.
Pb	54·47	54·46	53·5	77·5	76·52	49·34	49·93
Cl	19·03	18·68	20·2			17·16	17·13
CuO	20·27	20·93	16·5			17·18	17·05
H ₂ O	5·90	5·93	[5·5]	5·5	5·97	4·35	4·35
Residue.....	0·19	—	0·8	—	—	0·23	—
AgCl	—	—	1·6	—	—	11·59	11·54

Breunnerite.—Large rhombohedra have been observed by G. Piolti³ in serpentine near Avigliana. The mean value of the rhombohedron angle is $72^\circ 29' 42''$, whence $c = 0·808642$. The ordinary index of re-

¹ *Bull. Soc. franç. Min.*, 1906, **29**, 266.

² *Ibid.*, 14.

³ *Atti R. Accad. Sci. Torino*, 1906, **41**, 1066.

fraction determined by the Duc de Chaumes's method is 1.715. The composition is 90.47 per cent. MgCO_3 and 9.45 per cent. FeCO_3 . Traces of manganese are present, but no calcium. A specimen from the Sylvester mine, Val de Villé, analysed by Ungemach,¹ contained 3.10 per cent. CaCO_3 , 35.08 MgCO_3 , 61.25 FeCO_3 , whilst another specimen from the same mine contained 52.65 per cent. CaCO_3 , 25.47 per cent. MgCO_3 , and 21.85 per cent. FeCO_3 , and is therefore *ankerite*.

Two specimens from Frigido, near Massa, analysed by E. Manasse,² contained respectively 46.30 and 55.09 per cent. of FeO with 12.18 and 5.94 per cent. MgO . The former corresponds to $2\text{FeCO}_3, \text{MgCO}_3$, the latter to $5\text{FeCO}_3, \text{MgCO}_3$.

Two other specimens from Bottino, Tuscany, examined by the same analyst,³ had a composition agreeing with the formula $3\text{FeCO}_3, \text{MgCO}_3$.

Culverite.—A measurable crystal found on a specimen from Laurium has enabled A. Sachs⁴ to determine the constants of this mineral. He finds that it is monoclinic, $a:b:c = 0.82386:1:0.77672$; $\beta = 106^\circ 29'$. The composition of the apple-green crystals is as follows:

As_2O_5 .	NiO .	CoO .	FeO .	MgO .	H_2O .	Total.	Sp. gr.
40.45	26.97	trace	1.10	6.16	25.26	99.94	3.0104

The mineral is isomorphous with erythrite, though the similarity of angle is not very close.

Calcite.—In the course of an interesting investigation into the cause of the persistent phosphorescence exhibited by certain specimens of calcite from Fort Collins, Colorado, and from Joplin, Missouri, W. P. Headen⁵ has made a very careful analysis of the well-known yellow crystals from the latter locality. The results are as follows:

SiO_2 .	CO_2 .	CaO .	MgO .	MnO .	FeO .	ZnO .	Ce_2O_3 .
0.032	43.950	55.740	0.113	0.045	0.046	0.014	0.007
$(\text{Di}, \text{Sm}, \text{La})_2\text{O}_3$.				$(\text{Yt}, \text{Er})_2\text{O}_3$.			
0.012				0.012			

Traces of SO_3 , P_2O_5 , Cl , SrO , Al_2O_3 , Cr_2O_3 , NH_3 and Na_2O were observed, but no hydrogen sulphide could be detected, and of the gas evolved on dissolving 100 grams of material, all but 10 c.c. was absorbed by caustic potash. The author is inclined to attribute the remarkable phosphorescence to the presence of some member of the yttrium group. Specimens of other colours are found with the yellow ones, and those of

¹ *Bull. Soc. franç. Min.*, 1906, **29**, 279.

² *Mem. Soc. Tosc. Sci. Nat.*, 1906, **22**, 81.

³ *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, **15**, 20.

⁴ *Centr. Min.*, 1906, 193.

⁵ *Amer. J. Sci.*, 1906, [iv], **21**, 301.

purple tint exhibit the absorption bands characteristic of didymia, but none of them shows the persistent phosphorescence.

Celestine.—A dolomite containing considerable quantities of celestine is found at the Woolmitch quarry, near Maybee, Monroe County Michigan. Fine crystals of the mineral are met with in cavities in the rock, and have been the subject of crystallographic and chemical examination by E. H. Kraus and W. F. Hunt.¹ Axial ratio $a : b : c = 0.7781 : 1 : 1.2673$. Sp. gr. 3.979 at 20.5°. Analysis of clear, transparent crystals gave the following result:

SO ₃ .	SrO.	BaO.	MgO.	CaO.	(Al, Fe) ₂ O ₃ .	SiO ₂ .	Total.
43.58	53.75	1.26	0.12	0.45	0.15	0.22	99.53
43.60	53.78	1.32	0.14	0.47	0.13	0.23	99.67

Chalmersite.—E. Hussak,² having received a fresh supply of this mineral from the St. John del Rey mine, has been able to place 0.0896 gram of pure material in the hands of G. Florence for a new analysis, the first having been made on 0.016 gram only. The results quoted below lead to the formula CuFe_2S_3 or $\text{Cu}_2\text{S}, \text{Fe}_4\text{S}_5$.

Fe.	Cu.	S.	Total.
43.13	22.27	35.11	100.51

Clintonite and Chlorite Group.—E. Manasse³ has analysed a *chloritoid* (I) from Strettoia, Alpi Apuane, two specimens of *ripidolite*, from Calci (II) and Verruca (III) respectively, and a *clinocllore* from Affaccata (IV). The results are given below:

	SiO ₂ .	TiO ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	Na ₂ O.	H ₂ O.
I.	25.70	0.69	36.95	—	23.44	6.12	—	6.31
II.	26.14	—	28.65	—	18.38	19.48	0.56	11.93
III.	24.93	—	21.80	—	28.08	12.82	trace	11.64
IV.	28.95	—	21.41	3.12	—	34.07	—	12.86

In analysis I water was determined by ignition loss, and the iron all calculated as FeO, although Fe_2O_3 was also present.

Datolite.—A valuable contribution to our knowledge of this mineral has been made by E. H. Kraus and C. W. Cook,⁴ who have examined the excellent crystals found at Westfield, Massachusetts. These crystals are rich in faces, and exhibit monoclinic symmetry with the following constants, $a : b : c = 0.63482 : 1 : 1.26567$; $\beta = 90^\circ 9'$. Careful determinations of the specific gravities of four crystals gave a mean value of 3.0058 at 21.5°. This composition is accurately expressed by the accepted formula HCaBSiO_5 . Analyses II and III below were made on material derived from a single crystal. Under I is given the theoretical composition. Crystals of this mineral found at the

¹ *Amer. J. Sci.*, 1906, [iv], 21, 237. ² *Centr. Min.*, 1906, 332.

³ *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, 15, 20.

⁴ *Amer. J. Sci.*, 1906, [iv], 22, 21.

Colebrook mine, Dundas, Tasmania, have been measured by C. Anderson,¹ who finds that they have the composition given under IV.

	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	B ₂ O ₃ .	H ₂ O.	Total.
I.	37·63	—	—	34·95	—	21·81	5·61	—
II.	37·60	0·10	0·14	34·64	0·32	21·76	5·67	100·23
III.	37·58	0·10	0·16	34·74	0·31	21·94	5·76	100·59
IV.	36·28	—	0·95	35·21	—	20·48	6·48	99·40

Dundasite occurs in white spherical aggregates or in tufts of radiating silky needles associated with allophane and cerussite at Welsh Foxdale Mine, Trefriw, Carnarvonshire. G. T. Prior² finds that the analytical results suggest the formula, $\text{PbO}, \text{Al}_2\text{O}_3, 2\text{CO}_2, 4\text{H}_2\text{O}$:

PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CO ₂ .	H ₂ O > 100°.	H ₂ O at 100°.	Insol.	Total.	Sp. gr.
43·20	21·39	1·61	16·45	13·60	1·41	1·80	99·46	3·25

The Welsh mineral is like that from Tasmania, and shows a relation to dawsonite, $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{CO}_2, 2\text{H}_2\text{O}$.

Fluorite.—In the course of an elaborate study of fluorescence, H. W. Morse³ has examined the composition of the gases given off when fluorite is heated. In the case of specimens from Weardale these consisted chiefly of carbon monoxide, carbon dioxide, hydrogen, and nitrogen, with small quantities of oxygen. The two latter were not present in the proportions in which they occur in air, and no argon or helium was found. He concludes that the gases are due to the decomposition of some organic colouring matter, but that there is nothing to show that organic substances have anything to do with the fluorescence or thermo-luminescence of the mineral.

Garnet.—The chemical composition and optical constants of a number of garnets have been determined by M. Seebach.⁴ His results are tabulated below:

- I. Grossular from Xalostoc, Mexico. Pink dodecahedra.
- II. Pyrope from Colorado River, Arizona. Blood-red masses.
- III. Pyrope from Meronitz, Bohemia. Dark, wine-red grains.
- IV. Almandine from Ceylon. Brown-red to wine-red grains.
- V. Almandine from Jeypoor. Irregular, dark-red fragments.
- VI. Melanite from Frascati. Well-developed, black crystals.
- VII. Andradite from Dognaczka. Green crystals.
- VIII. Demantoid from Polewskoi-Zawod, Urals. Rolled masses.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Total.
I.	40·79	—	21·70	—	0·18	0·43	1·07	35·63	0·39	100·19
II.	43·37	—	20·99	2·36	—	10·21	0·52	4·54	18·42	100·41
III.	42·98	—	21·34	2·06	0·95	7·80	0·50	4·47	20·67	100·77
IV.	37·25	—	19·43	—	3·29	35·45	1·24	2·51	1·13	100·30
V.	38·07	—	19·63	—	2·16	31·58	1·36	5·03	2·77	100·60
VI.	34·74	1·54	5·44	—	21·95	1·99	0·65	32·58	1·48	100·37
VII.	36·79	—	1·39	—	29·30	0·69	0·26	31·40	0·77	100·60
VIII.	35·37	—	1·54	1·32	28·89	0·52	0·34	32·26	0·21	100·45

¹ *Rec. Australian Mus.*, 1906, **6**, 133.

² *Min. Mag.*, 1906, **14**, 167.

³ *Proc. Amer. Acad.*, 1906, 587.

Inaug. Diss. Heidelberg, 1906.

All the above are the mean of two concordant analyses, with the exception of VI, which is the mean of four analyses. The minerals were decomposed by fusion with anhydrous boric acid, and the analyses conducted by the methods developed by Jannāsch and his pupils.

In the following table are given the specific gravities and optical constants of the minerals before fusion, the specific gravities and indices of refraction for sodium light (so far as the latter could be determined) after fusion, and the proportion of the fused mineral soluble in hydrochloric acid. The molecular ratios calculated from analyses III, V, and VII agree fairly well with those required by the garnet formula $R''_3R'''_2Si_3O_{12}$, but diverge considerably from the theoretical values in the case of analyses IV, VI, and VIII.

No.	Before fusion.				After fusion.		
	Sp. gr.	μ_{Li} .	μ_{Na} .	μ_{Ti} .	Sp. gr.	μ_{Na} .	Percentage soluble in HCl.
I.	3·506	1·7319	1·7364	1·7411	2·866	1·6205	all
II.	3·715	1·7371	1·7417	1·7463	3·190	—	82
III.	3·679	1·7417	1·7463	1·7505	3·251	—	84
IV.	4·040	1·7724	1·7779	1·7825	3·009	—	72
V.	4·025	1·7763	1·7815	1·7862	3·240	—	74
VI.	3·774	1·8471	1·8560	1·8658	3·263	1·7667	97
VII.	3·660	1·8763	1·8878	1·8990	3·171	1·8177	all
VIII.	3·801	1·8767	1·8884	1·8999	3·335	1·8110	99

A few other analyses of garnet may also be recorded here. Of these I refers to a bright red *spessartite* from Kårarfvet near Falun, analysed by C. Benedicks¹; II gives the composition of a brown variety from the same locality; these garnets are interesting because they contain an appreciable quantity of yttria; III is a dark brown garnet found in pegmatite at Yamanō, Hitachi Province, Japan; IV occurs in brown-red crystals in mica andesite at Anamushi, Yamato Province. The analyses were made by Shimizu.²

	SiO ₂ .	Al ₂ O ₃ .	Yt ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
I.	35·67	22·50	1·19	19·17	21·91	traces	—	100·44	4·197
II.	35·36	22·34	1·23	22·01	18·80	traces	—	99·74	4·068
III.	36·39	23·05	—	24·77	14·21	1·57	0·67	100·66	—
IV.	36·74	20·71	—	34·91	1·67	2·11	3·27	99·41	—

Geikielite.—A number of specimens of ferro-magnesian titanates from Ceylon, including the original geikielite (analysis I below), have been examined by T. Crook and B. M. Jones.³ They find that this mineral contains a greater percentage of iron than was at first recorded, and they suggest that the formula should be written (Mg,Fe)TiO₃. The analyses II to X indicate a passage to picroilmenite, the composition of the latter being given under XI and XII.

¹ *Bull. Geol. Inst. Univ. Upsala*, 1906 (for 1904–5), 7, 271.

² *Beiträge z. Min. Japan*, 1906, No. 2, 53.

³ *Min. Mag.*, 1906, 14, 160.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
TiO ₂ ...	63.77	64.41	64.78	60.02	60.87	61.60	62.25	63.94	64.03	62.49	57.64	56.08
FeO	6.34	5.44	5.92	5.81	6.03	7.79	11.58	10.09	12.14	10.70	16.57	24.40
Fe ₂ O ₃ ..	1.98	2.77	2.22	6.80	5.69	4.95	—	0.25	—	3.54	10.17	5.43
MgO ...	28.50	27.90	27.90	27.79	27.29	26.81	26.08	25.79	24.66	23.60	15.56	14.18
	100.54	100.52	100.82	100.42	99.88	100.65	99.86	100.07	100.83	100.33	99.94	100.09
Sp. gr.	—	3.97	3.89	3.79	3.87	3.90	3.91	4.01	4.11	4.01	4.17	4.25

Glaserite.—It has been maintained on the one hand that a double salt of potassium and sodium sulphate exists of the constant composition $K_3Na(SO_4)_2$, so-called glaserite. On the other, it has been held that this name merely covers those members of the isomorphous series of mixed crystals formed by the two sulphates which contain a maximum of potassium sulphate. J. H. van't Hoff and H. Barschall¹ have investigated this point and find no evidence in support of the view that glaserite has a constant composition.

Gyrolite.—This rare mineral has been observed by E. Hussak² in the form of spherical aggregates composed of thin radial leaflets occurring in crevices in diabase at Mogy-guassu, São Paulo, Brazil. The specific gravity is 2.409, and the mineral is uniaxial with negative double refraction. The composition is very similar to that of gyrolite from Skye, as shown by the following analysis of white material made by G. Florence :

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
52.77	0.73	33.04	0.35	0.41	12.58	99.88

Under alumina is included a trace of ferric oxide. A dark green variety contained 7.36 per cent. $Fe_2O_3 + Al_2O_3$ and 0.32 per cent. MnO. We may note here that F. Cornu³ identifies gyrolite from the Hebrides, Faroë Islands, Greenland, Poonah, and São Paulo with the mineral described by Pelikan under the name zeophyllite.

Hellandite has already been the subject of a preliminary notice by W. C. Brögger, who has now⁴ published a full account based on the study of more than forty crystals. The mineral was found in a quarry opened in a pegmatite vein on the top of a small hill called Lindvikskollen near Kragerö, Norway. The crystals belong to the prismatic class of the monoclinic system, and are for the most part a good deal altered. The freshest consist of nut-brown material with vitreous lustre; others exhibit various shades of brown, while the most altered ones consist of a yellow to white earthy mass. The alteration, which is probably due to hydration, does not seem to have had any very great influence on the relative proportions of the constituents. The purest material had the specific gravity 3.67 to 3.70, that of the substance used for analysis II was 3.41 to 3.33. An analysis (I) by O. N. Heidenreich made on a small quantity of material has already

¹ *Zeit. physikal. Chem.*, 1906, **56**, 212.

² *Centr. Min.*, 1906, 330.

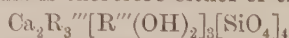
³ *Centr. Min.*, 1906, 79.

⁴ *Zeit. Kryst. Min.*, 1906, **42**, 417.

been published, II and III are due to L. Andersen-Aars; the material used for III was highly altered:

	SiO ₃	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	Ce ₂ O ₃	Y ₂ O ₃	Er ₂ O ₃	ThO ₂
I.	23.55	10.22	2.64	5.69	40.12			
II.	23.66	10.12	2.56	5.91	1.01	19.29	15.43	0.62
III.	27.88	9.67	2.01	3.13	0.37	19.71	13.26	0.30
	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.		
I.	10.05	—	0.26	0.06	7.55	100.19		
II.	9.81	0.10	0.23	0.06	11.75	100.55		
III.	9.97	0.13	0.41		13.09	99.93		

Since some 6 per cent. of the water was expelled below 500° and the rest only at red heat, it seemed probable that about 5 per cent. was chemically combined. This was confirmed by an experiment on the freshest material, when 4.86 per cent. of water was found. Accepting this value as the true percentage of water, and assuming that the small quantities of potash and soda are due to felspar, the ratios (calculated from II) R''O : H₂O : R₂'''O₃ : SiO₂ are very accurately 2 : 3 : 3 : 4. The formula is therefore either of the type



or of the type $\text{Ca}_2[\text{R}'''(\text{OH})]_6[\text{SiO}_4]_4$. Of these two possibilities, Brögger is inclined to prefer the first on the ground of certain analogies which hellandite shows with guarinite, danburite, andalusite, and topaz. Accepting this view, the composition of the mineral may be represented thus: $\text{Ca}_2[\frac{2}{3}\text{Al}_2(\text{Mn,Fe})]_3[(\text{Y,Er,Ce})(\text{OH})_2]_3[\text{SiO}_4]_4$.

Hibschite.—Reference was made to this mineral last year. A detailed account of its properties and mode of occurrence has recently been published by F. Cornu.¹

Huebnerite.—Large black crystals from the Comstock mine, Lawrence County, South Dakota, were found by W. P. Headden² to have the following composition:

WO ₃	MnO.	FeO.	CaO.	Total.
75.12	20.54	3.01	1.04	99.71

Jadzite and Nephrite.—Some very valuable contributions to our knowledge of these two minerals are to be found in the monumental treatise entitled "Investigations and Studies in Jade,"³ issued by the executors of Reginald Heber Bishop. In two vast volumes, each weighing about sixty pounds, are embodied the results of a series of studies by leading American experts of the specimens contained in the great Bishop collection now preserved in New York. The mineralogical portion has been edited by G. F. Kunz, and he has had the assistance of S. L. Pentfield, F. W. Clarke, J. P. Iddings, C. Palache, L. V. Pirsson, and others. On breaking up a specimen of jadeite, which

¹ *Tsch. Min. Mitt.*, 1906, **25**, 249.

² *Proc. Colorado Sci. Soc.*, 1906, **8**, 174.

³ *Privately printed*, New York, 1906.

probably came from Tibet, two small crystals were found. These closely resembled augite in shape, and enabled Penfield to determine the crystallographic constants of the mineral. He found $a:b:c = 1.103:1:0.613$; $\beta = 72^\circ 44\frac{1}{2}'$. The cleavage angle was $92^\circ 58'$. The extinction angle measured on (010) was 34° and the optic axis angle 70° , one axis being nearly parallel to the Z axis of the crystal. This specimen had the following composition:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.	Sp. gr.
58.80	25.37	0.33	0.25	0.58	14.65	0.05	0.14	100.17	3.3359

In all, fifty-eight analyses of the two minerals are given, and, with two exceptions, these were made by P. T. Walden and H. W. Foote. In his discussion of the formulæ to be assigned to these minerals, F. W. Clarke advances arguments in support of the view that the molecules of the pyroxenes are more complex than those of the amphiboles, and that jadeite must be represented as $\text{Na}_6\text{Al}_6\text{Si}_{12}\text{O}_{36}$. Further, he holds that it is not to be regarded as a metasilicate, but as a mixture of an orthosilicate and a trisilicate. At the conclusion of a paragraph devoted to a discussion of the origin of jadeite considered as a rock, Pirsson says "jadeite is a metamorphosed igneous rock, a member of the phonolite family. The white varieties are probably metamorphosed dikes of the aplitic, leucocratic type, belonging in this family and the darker green types those containing more iron-bearing dark silicates, like tinguaites." The mean value of the specific gravity of all the nephrite specimens was 2.9505; that of the jadeites, including some chloromelanites, was 3.3202.

Janosite.—The existence of this mineral as a separate species has been denied by E. Weinschenk,¹ who on the ground of its optical properties has identified it with copiapite. H. Böckh and K. Emszt, the discoverers of janosite, have, however, reiterated their belief in its individuality, laying special stress on its specific gravity and chemical composition. In his reply Weinschenk states that a comparison of janosite with specimens of copiapite recently received from Copiapo fully confirms his previous conclusion. Further, a specimen of janosite supplied by Böckh was found to contain 30.80 per cent. Fe_2O_3 and to have a specific gravity 2.17, the corresponding values found for copiapite being 31.09 and 2.19 respectively.

Jamesonite.—Imperfect crystals occurring in quartz veins at Sheridan, Pennington County, South Dakota, have been analysed by W. P. Headden.² The percentages found are in tolerable harmony with those required for the ordinarily accepted formula, $2\text{PbS}, \text{Sb}_2\text{S}_3$:

S.	Sb.	Pb.	Fe.	Cu.	Zn.	Co.	Insol.	Total.	Sp. gr.
18.90	26.99	51.15	1.30	0.24	0.05	trace	1.13	99.76	5.81304

¹ *Ann. Report*, 1905, 279; *Föld. Közlemény*, 1906, **36**, 224, 228, 359.

² *Proc. Colorado Sci. Soc.*, 1906, **8**, 174.

Malacon.—A specimen of this mineral examined by E. S. Kitchin and W. G. Winterson¹ proved to be distinctly radioactive and to contain argon. Taking the radioactivity of uranium oxide as unity, that of the malacon is 0.0161. This value is much greater than can be accounted for by the uranium present in the mineral. After decomposition the radioactivity is entirely associated with the zirconium dioxide. On fusion with potassium hydrogen sulphate, 100 grams of malacon gave 37.91 c.c. of gas, consisting of 33.24 c.c. of carbon dioxide, 2.82 c.c. of argon, 0.94 c.c. of helium, 0.57 c.c. of hydrogen, and 0.34 c.c. of nitrogen. The specific gravity is 3.908, rising to 4.232 after heating. The complete analysis is as follows :

ZrO ₂ .	SiO ₂ .	Fe ₂ O ₃ .	MgO.	CaO.	U ₃ O ₈ .	(Y,Ce) ₃ O ₈ .	H ₂ O.
67.78	22.53	4.93	0.70	0.41	0.33	0.09	1.84

If the other constituents are neglected, and zirconia and silica calculated to 100, the percentages obtained agree well with those required for the formula $\text{Zr}_3\text{Si}_2\text{O}_{10}$. The analytical results differ a good deal from those previously recorded for the substance, and from which the formula $3(\text{ZrO}_2, \text{SiO}_2), \text{H}_2\text{O}$ has been derived.

Meneghinite.—A fibrous mineral found in the Gorham claim near Rochford, Pennington County, South Dakota, has been analysed by W. P. Headden.² The ratios obtained are only approximate, but show that the probable formula is $4\text{PbS}, \text{Sb}_2\text{S}_3$:

S.	Sb.	Pb.	Cu.	Insol.	Total.	Sp. gr.
17.51	18.20	62.85	0.86	0.49	99.91	6.21

Traces of As, Bi, Cd, and Fe are also present.

Naegite.—T. Wada³ has published some important fresh information about this mineral. He states that a crystallographic examination by Takimoto has shown that in habit and angles the mineral is closely related to zircon, whilst Haga has found that it contains a large quantity of zirconia, a constituent previously overlooked, probably owing to some imperfection in the methods of separation employed. Haga's analysis is as follows :

ZrO ₂ .	ThO ₂ .	SiO ₂ .	(NbTa) ₂ O ₅ .	UO ₃ .	Y ₂ O ₃ .	Total.	Sp. gr.
55.30	5.01	20.58	7.69	3.03	9.12	100.73	4.091

Petterdite.—Under this name there was described, a few years ago, a mineral from the Britannia mine, Zeehan, Tasmania, which was supposed to be a new oxychloride of lead. A careful re-examination of this substance recently made by C. Anderson⁴ has proved that it is merely a variety of mimetite.

¹ *Trans.*, 1906, **89**, 1568.

² *Proc. Colorado. Sci. Soc.*, 1906, **8**, 174.

³ *Beiträge z. Min. Japan*, 1906, No. **2**, 23.

⁴ *Rec. Australian Mus.*, 1906, **6**, 133.

Pitchblende.—The pitchblende from which rutherfordine is derived (see p. 310) is 20 per cent. more radioactive than that from Joachimsthal, and has been shown by W. Marekwald¹ to have the following composition :

U ₃ O ₈ .	PbO.	CaO.	FeO.	SiO ₂ .	H ₂ O + CO ₂ .	Gangue.
87.7	7.5	2.1	1.0	0.3	0.5	0.2

Plumbogummite.—E. Hussak² has published the following analysis by G. Florence of a mineral found in the form of pebbles, "favas," in the diamond sands of Brazil :

SiO ₂ .	PbO.	CaO.	CeO.	Al ₂ O ₃ .	P ₂ O ₅ .	H ₂ O.
0.70	35.50	0.62	0.16	24.92	22.50	16.30

The corresponding formula, 2(Pb,Ca)O, 3Al₂O₃, 2P₂O₅, 10H₂O, is near to that of plumbogummite, although it contains 3 molecules more water.

Pyrochroite.—This rare mineral occurs at Långban in prisms and needles with a distinct basal cleavage. The following analysis, given by H. Sjögren,³ agrees with the formula Mn(OH)₂ :

MnO.	FeO.	CaO.	MgO.	H ₂ O.	Sp. gr.
77.3	0.4	trace	1.7	20.9	3.2435

Quartz.—J. G. Königsberger and W. J. Müller⁴ have studied the liquid inclusions in quartz crystals from the biotite-protogine of the Aar district. They find that for these crystals there is a constant relation between the volume of the liquid and the volume of the gas in a cavity, a fact first observed by Sorby. On heating at from 200° to 230° the bubbles disappear, the liquid expanding to fill the cavity. They conclude that the included matter represents a homogeneous portion of the liquid phase. Its composition in the case of a specimen from the Bächistock appears to be as follows :

H ₂ O.	CO ₂ .	Na.	K.	Li.	Ca.	Cl.	SO ₄ .	CO ₃ .
83.4	9.5	2.0	0.7	0.2 ?	0.3	1.6	0.5	1.8

M. Berthelot⁵ has found that crystals of amethyst from Brazil decolorised by heating to 300° regain their original tint on exposing them for a few weeks to the action of radium chloride. He attributes this change to the reoxidation of traces of manganese present, and suggests that the colour of amethyst and other minerals may be due to the action of radioactive substances. On heating smoky quartz and green fluor spar, petroleum is driven off, and in these cases the colour is due to organic matter.

Rhodochrosite.—Small rhombohedra {100} of this mineral have been

¹ *Centr. Min.*, 1906, 761.

² *Tsch. Min. Mitt.*, 1906, 25, 335.

³ *Geol. Fören. Stockholm Förhandl.*, 27, 37.

⁴ *Centr. Min.*, 1906, 72.

⁵ *Compt. rend.*, 1906, 143, 477.

found at S. Barthélemy, Val d'Aosta, by F. Millosevich.¹ The cleavage angle is $73^{\circ}10'$, and the composition as follows:

MnO.	FeO.	CaO.	MgO.	CO ₂ (diff.).
56.00	2.04	3.33	trace	38.63

Rock Salt.—The blue colour observed in certain specimens of rock salt has been the subject of much experiment and speculation in recent years. As pointed out in a paper by F. Focke and J. Bruckmoser,² the explanations offered fall under three main headings. In the first place, it is held that the phenomenon is a purely physical one due to the presence of very minute fissures, secondly we have the view that it is due to the presence of some inorganic colouring matter such as the subchloride of sodium or a compound of iron, and lastly that it is caused by organic material. It has, however, been shown that the blue colour can be produced by exposing salt to the action of cathode rays or by heating it with metallic sodium, and the opinion is now widely held that the colour is due to the presence of subchloride or of metallic sodium. Though the latter view does not commend itself to Focke and Bruckmoser or to E. Pieszczyk,³ who has found a deficiency of chlorine amounting to as much as 0.4 per cent. in the blue portions, it has received strong support from the work of H. Siedentopf.⁴ This author investigated specimens of salt, coloured blue by the action of sodium vapour with the aid of the ultra-microscope and believes that he has demonstrated the presence of metallic sodium deposited in ultra microscopic fissures in the salt. These particles of sodium may possibly be covered by a very thin or "molecular" coating of subchloride which protects them from the action of reagents such as chlorine. He thinks that since rock salt strongly absorbs Becquerel rays the blue colour of the mineral may perhaps be due to the sodium produced by the cumulative effect of the radiation absorbed during long periods of time.

The gases included in certain specimens of salt from Roumania have been the subject of an interesting investigation by N. Costachescu.⁵ The gases were extracted either by dissolving the salt in well boiled water or by pulverising it under mercury. The composition of the gases was found to vary a good deal with the method of extraction employed, but the following points appear to be established. In the first place the quantity of gas contained in a given weight of salt varies greatly, but there is no relation between the quantity of gas evolved and the solid impurities in the salt. Secondly, as regards the nature of the gases given off, the specimens examined fall into two groups, those in which hydrocarbons are predominant and those which yield little else

¹ *Atti R. Accad. Lincei*, 1906, [v] 15, i, 317.

² *Tsch. Min. Mitt.*, 1906, 25, 43.

³ *Pharm. Zeit.*, 51, 700.

⁴ *Phys. Zeit.*, 1905, 6, 8 5.

⁵ *Ann. Sci. Univ. Jassy*, 1906, 4, 3.

but nitrogen, a gas which is invariably present. Oxygen is also always found, but in smaller proportion than the nitrogen and there is no constant relation between the quantities of these two elements. Carbon dioxide is either absent or occurs in very small quantities. Argon could not be detected. Methane is almost always present, but the higher hydrocarbons appear to be absent. To account for these facts the author suggests that the gases have been derived mainly from the decomposition of the microscopic fauna of the lagoon in which the deposits were laid down, and to but a limited extent from the atmosphere through the medium of the solvent. The absence of carbon dioxide and argon can be explained in this way, but it is difficult to account satisfactorily for the oxygen always observed.

Sarcolite.—Specimens of this mineral from Vesuvius have been submitted to a careful crystallographic and optical examination by A. Pauly.¹ Two pure crystals were used for analysis :

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.	Sp. gr.
39·34	21·63	33·70	0·36	4·43	traces	99·46	2·7

Scheelite.—The crystals from Traversella have been measured by L. Colomba² who moreover has analysed specimens of different colours in order to test Traube's hypothesis that the ratio $a : c$ varies with the amount of molybdic acid present. His results are as follows :

	WO ₃ .	MoO ₃ .	CaO.	MgO.	Total.	$a : c$.
I. Colourless crystals	77·03	3·15	19·73	—	99·91	1·5398
II. Reddish-brown crystals ...	77·35	2·46	18·33	1·67	99·81	—
III. Greenish-brown „ ...	78·75	1·47	19·23	0·55	100·00	1·5352
IV. Orange „ ...	79·68	0·72	19·43	trace	99·83	—

Since the mean value of c calculated from measurements of crystals of the composition given under I and III falls about midway between those accepted by Traube for pure scheelite and pure calcium molybdate respectively, this work affords no confirmation of the view that a regular variation takes place.

Siderite.—Minute crystals from Frostburg, Maryland, have been shown by W. T. Schaller³ to be pure ferrous carbonate. An analysis made on 0·1 gram of carefully selected material gave 62·01 per cent. of iron (calc. 62·07 per cent.). MnO, CaO, and MgO were proved to be absent. A number of measurements of the crystals were made for the purpose of defining accurately the ratio $a : c$ for pure siderite. The mean value deduced is $c = 0·8241$. This corresponds to a cleavage angle $rr' = 73^\circ 18' 6''$ and differs considerably from that hitherto adopted for the mineral, namely, $c = 0·81841$, $rr' = 73^\circ 0'$.

¹ *Centr. Min.*, 1906, 266.

² *Atti R. Accad. Lincei*, 1906, [v], 15, i, 281.

³ *Amer. J. Sci.*, 1906, [iv], 21, 364.

Stibiotantalite.—This very rare mineral was originally described by G. A. Goyder as occurring in water-worn fragments at Greenbushes, Western Australia. Crystals have been discovered in recent years at Mesa Grande, San Diego County, California, associated with tourmaline, pink beryl, quartz, orthoclase, and lepidolite, and have been the subject of an exhaustive investigation by S. L. Penfield¹ and W. E. Ford. The mineral is an isomorphous mixture of $(\text{SbO})_2\text{Cb}_2\text{O}_6$ and $(\text{SbO})_2\text{Ta}_2\text{O}_6$, and has a specific gravity varying from 5.98 to 7.37, depending on the relative proportions of columbium and tantalum present, and diminishing as the amount of the latter decreases. It crystallises in the hemimorphic class of the orthorhombic system, though owing to twinning the crystals simulate holohedral symmetry. In axial ratio and habit it shows relations with columbite. Owing to its yellow colour, high index of refraction, and good cleavage it might be mistaken for blende. In the following table I is the original analysis of the Australian mineral, II and III are each the means of two concordant analyses made on separate crystals of the Mesa Grande material.

	$(\text{Ta,Cb})_2\text{O}_5$	Sb_2O_3	Bi_2O_3	NiO	H_2O	Total	Sp. gr.
I.	58.69	40.23	0.32	0.08	0.08	99.90	7.37
II.	55.33	44.26	0.33	—	—	99.92	6.72
III.	50.30	49.28	0.53	—	—	100.11	5.98

Tapiolite.—A group of distorted crystals found by W. P. Headden² in granite near Custer City, South Dakota, were shown by S. L. Penfield to be tetragonal pyramids {111} with small {201} planes. Two analyses were made :

	FeO	Ta_2O_5	Cb_2O_5	WO_3	SnO_2	Cassiterite.	Insol.	Total.
I.	16.85	78.61	4.29	0.11	0.07	0.31	—	100.24
II.	15.60	78.58	3.90	0.59		—	1.29	99.96

Traces of TiO_2 were found in analysis I and there is reason to believe that FeO is too high. The formula is FeTa_2O_6 , a portion of the tantalum being replaced by columbium and taken in conjunction with the crystallographic characters shows that the substance is tapiolite. The specific gravity 7.2185 is low for a compound containing so little columbic acid. This point is discussed by Headden, who finds himself unable to explain it.

Tetrahedrite.—In the course of a description of the mines and minerals of the Val de Villé (Weilerthal), Alsace, Ungemach³ has given the results of an elaborate crystallographic investigation of the beautiful crystals of tetrahedrite found at the Sylvester mine. Two different types of crystals can be readily distinguished. One (analysis I below), rich in arsenic but poor in silver, is met with in the upper portions of the veins; the other, found at greater depths, is rich in silver and poor in arsenic (analysis II).

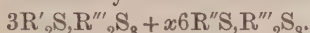
¹ *Amer. J. Sci.*, 1906, [iv], 22, 61.

² *Proc. Colorado Sci. Soc.*, 1906, 8, 177.

³ *Bull. Soc. franç. Min.*, 1906, 29, 194.

The comparatively large quantities of Zn and Bi present are somewhat remarkable, and the author is inclined to believe that they are due to the presence of native bismuth and of zinc blende. Be this as it may, if the formula is calculated omitting zinc, it is found that the ratio $R''S : R_2'''S_3$ is 3.07 : 1 for I and 3.21 : 1 for II.

The variety of tetrahedrite previously described under the names *coppite* and *frigidite* has been examined by E. Manasse.¹ Three specimens were analysed. The results, which are given below, analyses III, IV, and V, are in harmony with a formula of the type



Traces of tin were found in IV and V.

	Cu.	Ag.	Pb.	Fe.	Zn.	Ni.	As.	Sb.	Bi.	S.	Total.	Sp.gr.
I.	38.15	trace	0.53	3.77	5.05	—	6.75	17.47	1.63	25.58	98.93	4.82
II.	34.15	5.94	—	3.79	4.86	—	1.21	25.24	—	25.22	100.41	5.10
III.	37.42	—	trace	6.60	1.72	0.23	trace	29.28	—	25.70	100.95	—
IV.	37.54	—	trace	6.01	1.98	0.14	trace	29.54	—	25.48	100.69	—
V.	30.04	—	0.26	9.83	0.59	3.46	1.50	28.82	—	24.48	98.98	—

Thuringite.—F. Kretschmer² has published further details as to the occurrence of this mineral at Gobitschau, and has given three new analyses.

Thorianite.—In a paper published last year, W. R. Dunstan and G. S. Blake suggested that the intimate association of thorium with oxides of uranium might be a case of isomorphous mixture. This view has been confirmed by a series of analyses of thorianite from the Galle district of Ceylon, recently published by W. R. Dunstan and B. M. Jones.³ Their results show that the proportion of the two oxides present in the mineral may vary considerably, as can be seen on comparing columns I to VII of the following table. I gives the composition of small crystals from Hinidumpattu, Galle District; II to VI that of large lumps from the same locality, II, III and IV being different portions of the same crystal; VII is an analysis of a large crystal of the ordinary variety from Balangoda. All the specimens contained helium and carbon dioxide. The radio-activity of specimen I was compared by R. J. Strutt with that of the mineral the composition of which was given last year and found to be 1.16 times as great. Column VIII contains some determinations of the more important constituents of thorianite made by E. H. Büchner⁴ in Sir W. Ramsay's laboratory in the course of an investigation into the distribution of the radioactivity among the constituents of the mineral. In addition to the elements enumerated, small quantities of copper, tin, antimony, bismuth (?), aluminium, titanium, and zirconium were estimated, and traces of mercury, arsenic (?), cadmium (?) and phos-

¹ *Mem. Soc. Tosc. Sci. Nat.*, 1906, **22**, 81.

² *Centr. Min.*, 1906, 309.

³ *Proc. Roy. Soc.*, 1906, **77**, A, 546.

⁴ *Ibid.*, **78**, A, 385.

phorus observed. One gram of the mineral yielded 8.2 c.c. of helium. The radioactivity is associated almost entirely with the portion of the mineral soluble in nitric acid.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
ThO ₂	58.84	62.16	66.82	{ —	62.32	63.36	78.98	70.96
(Ce, La, Di) ₂ O ₃	0.85	1.84			2.24	1.16	1.47	1.96
UO ₂	32.74	{ 10.32 18.88 }	28.24	28.68	27.02	27.99	13.40	13.12*
UO ₃								
PbO	2.56	2.29	2.29	2.50	2.99	2.90	2.54	2.42
Fe ₂ O ₃	1.31	1.11	1.22	2.43	2.28	1.27	0.87	2.05
CaO	0.19	0.59	0.54	—	0.50	0.85	0.91	0.13
H ₂ O	1.26	1.05	1.00	—	2.16	1.32	1.28	3.20
Insol. in HNO ₃	0.45	0.77	0.56	0.54	0.87	0.77	0.47	—

* U₃O₈.

Titanite.—F. Zambonini¹ called attention last year to the unsatisfactory state of our knowledge of the composition of titanite. He has recently returned to this question, and has pointed out that the composition of specimens containing tervalent elements is better expressed by Blomstrand's formula, $2(R_1''R_2'''O_2, TiO)O, SiO_2$, than by that due to Groth, who regards such titanites as consisting of isomorphous mixtures of CaTiSiO₅ and R₂'''SiO₅. Blomstrand's formula represents titanite as containing titanyl, TiO, playing the part of a cation thus, TiO:O₂SiO₂:Ca, aluminium, iron, yttrium, and cerium entering the molecule in the bivalent grouping R₂'''O₂. As, however, recent work on titanium, zirconium, and tin has shown that these elements readily form complex anions, Zambonini thinks that it will be more in harmony with what is known of the general chemical character of titanium if it is regarded as playing a similar part in titanite. He therefore proposes to modify Blomstrand's formula in this sense, and regards the mineral as the calcium salt of a complex silicotitanic acid TiO:SiO₄:Ca. The tervalent elements enter the molecule as two univalent groupings R'''O, replacing TiO.

Zeolites.—Certain zeolites which occur in the amygdaloidal basalt of the Debaroa plateau, Eritrea have been described by E. Manasse.² Two specimens of *chabazite* had a composition agreeing with the formula CaAl₂Si₄O₁₂.6H₂O. Analyses I and II. Crystals of *apophyllite*, measured by G. D'Achiardi, agreed approximately with the formula H₇KCa₄(SiO₃)₈.4½H₂O. Analysis III. The loss of water at various temperatures and its reabsorption on standing in moist air were studied in the case of both minerals.

E. Manasse³ has also re-examined the mineral from Montecatini termed *picrothomsonite* by Meneghini and A. D'Achiardi, and has come to the conclusion that it is *thomsonite*. The mean composition derived from two concordant analyses is given under IV below. Associated with

¹ *Atti R. Accad. Lincei*, 1906, [v], 15, i, 291.

² *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, 15, 65.

³ *Ibid.*, 20.

this substance is another called *sloanite* by Meneghini. This appears to be identical with *natrolite*. Analysis V.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	48·35	19·47	8·77	0·20	trace	1·05	22·13	99·97
II.	46·69	20·27	9·72	—	trace	0·96	22·80	100·44
III.	52·84	trace	24·46	—	5·42	trace	16·48	99·20
IV.	36·90	31·36	14·48	0·33	0·65	3·81	13·59	101·12
V.	46·49	25·47	1·10	trace	trace	17·05	9·76	99·87
VI.	65·21	11·20	3·77	trace	6·07		14·22	100·47

G. D'Achiardi¹ has referred to *ptilolite*, a mineral from San Piero in Campo, Elba, which has the composition given under VI, and has suggested that the mineral called *hydrocastorite* is possibly identical with a pulverulent form of *stilbite*, containing small quantities of lithium, which he has found at the same locality. He has also given some further account of the zeolite which was mentioned last year as probably constituting a new species.²

Zoisite.—Striated prisms associated with prehnite have been found at the Trace mine, Juarez district, Lower California. The optical characters have been studied by O. C. Farrington,³ and the mineral has been analysed by H. W. Nichols. Analysis I below.

The numbers obtained agree well with the formula $H_4Ca_4Al_6Si_6O_{27}$, which is that usually accepted for zoisite with the addition of one molecule of water. There is good evidence for believing that in this case the extra molecule of water is a primary constituent of the mineral, and not the result of alteration, and the authors quote other similar instances. Traces of K and Na were also present.

Analysis II, which agrees with the ordinary formula, was made by E. Manasse,⁴ on a specimen from Monte Corchia, Alpi Apuane.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MnO.	CaO.	MgO.	H ₂ O.	Total.
I.	33·15	29·50	4·60	0·55	22·71	0·63	3·76	99·90
II.	37·86	26·88	7·90	—	24·65	—	2·07	99·36

Radioactivity of Minerals.

The radioactivity of minerals containing thorium has occupied the attention of several workers.

B. B. Boltwood⁵ has examined thorianite, thorite, orangite, and monazite, containing 78·8, 52, 51·1, and 4·66 per cent. of ThO₂ respectively. He has found that the activity of one gram of thoria was practically the same in each of the four minerals. He believes that his results confirm the view that radio-thorium is a disintegration

¹ *Mem. Soc. Tosc. Sci. Nat.*, 1906, 22.

² *Ann. Report*, 1905, 282.

³ *Field Columbian Mus. Pub.*, 112; *Geol. Ser.*, 3, No. 4, 55.

⁴ *Proc. verb. Soc. Tosc. Sci. Nat.*, 1906, 15, 20.

Amer. J. Sci., 1906, [iv], 21, 415.

product of thorium, but that they do not lend any support to the idea that the activity of thorium in a mineral depends on the amount of uranium present. On the other hand, the available data point to the conclusion that the quantity of actinium in a radioactive mineral is proportional to the uranium present. Similar conclusions as to the proportionality existing between the activity of thorium minerals and their thorium content have been arrived at by H. M. Dadourian¹ and by H. N. McCoy and W. H. Ross.²

Finding reason to suspect that their former estimate of the amount of radium associated with a given quantity of uranium in a mineral was too high, E. Rutherford and B. B. Boltwood³ have repeated the estimation. They now find that approximately 3.8×10^{-7} grams of radium are associated with 1 gram of uranium, a result about half that previously obtained. They point out that a ton of 60 per cent. uranium ore would carry radium equivalent to about 0.35 gram of radium bromide.

Special Reactions of Minerals.

F. Cornu⁴ has examined and tabulated the behaviour of a large number of minerals when finely powdered, moistened, and brought in contact with neutral litmus paper. He finds that all the minerals of the kaolin and pyrophyllite groups show acid reaction, and that the same is true of opal. On the other hand, olivine, mesolite, and talc react alkaline. The same writer⁵ bases a method of distinguishing between calcite and dolomite on the behaviour of these substances towards water containing phenolphthalein. On shaking the solution with finely-divided calcite a dark red colour is produced, whilst dolomite gives merely a faint red tinge. V. Goldschmidt⁶ has called attention to the ease with which a number of minerals can be determined by finding the loss of weight they suffer on ignition. Experiments made under his direction by P. Hermann on a number of zeolites show that these substances can be rapidly identified by heating quantities of from 30 to 100 milligrams in a platinum spoon over a spirit lamp.

Meteorites.

The composition of a number of meteorites has been examined during the past year. Among these we may notice the following:

Cañon Diablo.—A septarian nodule found in this meteorite has been studied by W. Tassin.⁷ The septa are metallic and like the mass of

¹ *Amer. J. Sci.*, 1906, [iv], **21**, 427.

² *Ibid.*, 433.

³ *Ibid.*, 1906, **22**, 1.

⁴ *Tsch. Min. Mitt.*, 1906, **24**, 417.

⁵ *Centr. Min.*, 1906, 550.

⁶ *Jahrb. Min.*, 1906, i, 16.

⁷ *Proc. U.S. Nat. Mus.*, No. 1497.

the iron. The interseptal portions are made up of crystalline graphitic and amorphous carbon mixed with troilite. A lustrous metallic substance consisting mainly of iron (88.8 per cent.), but containing nickel, silicon, carbon, phosphorus, and a trace of cobalt, is also present.

Coon Butte.—This aerolite was discovered in 1905 by D. M. Barringer near Coon Butte, Coconino County, Arizona. There is some evidence to show that its fall was observed in January, 1904. Its general appearance and the results of an optical examination made by G. P. Merrill suggest affinities with the meteorites from Ness County, Kansas, or with the Pultusk meteorite. J. W. Mallet¹ has found that it consists mainly of enstatite and olivine, but it also contains maskelynite and nickel-iron. The composition of all these constituents has been ascertained, and traces of tin and copper found in the last.

Estacado.—An aerolite fell in 1882 near Estacado, on the staked plains of north-western Texas. It has been investigated by J. M. Davison,² who has determined the composition of the metallic portion, which amounts to 16.41 per cent., and of the stony matter, which appears to be mainly olivine and enstatite.

Kangra Valley.—An aerolite which is reported to have been seen to fall in the Kangra Valley, Northern Punjab, has been described by W. N. Hartley.³ The specimen, which weighs 350 grams, appears to consist of a crystalline ground mass of enstatite and olivine, through which are scattered numerous metallic grains. A spectroscopic examination of the metallic portion showed the presence of Fe, Ni, Co, Cr, with small quantities of Cu, Ag, Pb, and Ga. Traces of Mn, Ca, K, and Na were also detected. Ca and Mg are the principal constituents of the siliceous portion, accompanied by minute quantities of Fe, Ni, Cr, Ga, Sr, Pb, Ag, Mn, K, and Na.

Kodaikanal.—A new silicate, weinbergerite, has been discovered by F. Berwerth in this meteorite (see page 310).

Modoc.—A fall of meteorites took place on the night of September 2, 1905, in the vicinity of Modoc, a small town in Scott County, Kansas. Fourteen specimens, mostly complete individuals, have been recovered, and the largest of these, weighing 4.64 kilos, now in the possession of the U.S. National Museum, has been described by G. P. Merrill.⁴ Under the microscope it is seen to consist essentially of olivine and enstatite, with blebs of metallic iron and troilite. It belongs to Brezina's group of veined chondritic meteorites. Analyses of the metallic portion and of the soluble and insoluble silicates have been made by W. Tassin.

¹ *Amer. J. Sci.*, 1906, [iv], 21, 347.

² *Ibid.*, 186; 22, 55.

³ *Trans.*, 1906, 89, 1566.

⁴ *Amer. J. Sci.*, 1906, [iv], 21, 356.

Shelburne.—A second stone of this fall has been described by O. C. Farrington.¹

South Bend.—O. C. Farrington¹ has also examined a pallasite weighing $5\frac{1}{2}$ lb., found in 1893 near South Bend, St. Joseph County, Indiana, and refers it to the Imilac group. The ratio of nickel-iron to chrysolite is 21.4 to 78.6.

In conclusion, it should be noted that a great deal of interesting information regarding Japanese meteorites has been brought together by K. Jimbō.²

A. HUTCHINSON.

¹ *Field Columb. Mus. Pub.*, 109; *Geol. Ser.*, 3, 2.

² *Beiträge z. Min. Japan*, 1906, No. 2, 30.

RADIOACTIVITY.

THE year's work has been notable for the very large number of important investigations, with interesting theoretical bearings, but chiefly concerned with points of detail rather than with any great general extension of the boundaries of the subject. Radioactivity at the present time resembles somewhat the science of organic chemistry in its early days, both in its bewildering wealth of detail and in the opportunities it affords for the crucial examination of theoretical predictions. On this account, however, it becomes increasingly difficult to give any connected account of the progress made. The various investigations in different parts of the subject are so closely interconnected that they cannot well be separated into distinct sections, and some latitude in the order in which the subjects are taken must be allowed. It is impossible to draw a distinction between researches which are more nearly physical and those which are mainly of chemical interest, for it seems that the more clearly an investigation falls under the one head the more surely does it become indispensable to the other side of the subject. Thus the electro-chemical researches, particularly of von Lerch, on the separation of successive disintegration products are indispensable to physicists in the analysis of the complex radiations, and the determination of the physical constants of each type of radiation separately. Bragg's work on the ionisation ranges of the α -rays, dealt with at length last year,¹ has developed this year in the hands of Hahn into a method of analysis of two successive products hitherto regarded as single, and which so far chemical methods have proved powerless to separate. Rutherford's final results, to be considered at length, on the constants of the α -particle, threaten to raise again the problem of the atomic weights of the inert gases, and the validity of the theoretical grounds on which the accepted values are based, whilst Bragg's method of ionisation ranges, as already indicated, affords a novel and independent method of determining the atomic weight of gases. In the wealth of information concerning the properties of each of the new separate disintegration products, now become too numerous almost to remember, no detail is too unimportant to be dealt with, for at any moment some

¹ *Ann. Report* 1905, 295.

such apparently trivial fact may furnish a clue to the laws underlying the arbitrary and mysterious courses along which the devolution of matter is proceeding before our eyes. Already it is becoming increasingly evident that there is familiar method in the apparent madness, and in the strange resemblances and analogies between the successive members from different parent elements we have a new and varied phase of the old problem of the relations between the elements themselves which finds its most complete expression, although no explanation, in the Periodic Law. When it is considered that each of these disintegration products is a new elementary form of matter and that the total number of elements known has been increased by nearly one-fourth through the study of radioactivity in the last five years, we have a sufficient answer to the view the writer has heard expressed that radioactivity is outside the sphere of chemistry and must be considered the exclusive territory of the physicist. Since all the newcomers are derived from and related to two only of the previously known elements, it may be realised how little the possibilities of matter have been exhausted by the older chemistry. But the prospect of any simple and complete hypothesis of matter seems to have been rendered more remote rather than brought within measurable distance of realisation by the recent extensions.

Constants of the α -particle.—Some of the problems in connexion with the nature of the α -ray will be first considered, as these have again occupied a prominent place in the year's work. The controversy¹ between Becquerel on the one hand² and Rutherford³ and Bragg⁴ on the other has been satisfactorily settled. In a later communication, Becquerel⁵ gives the results of further experiments in which a beam of α -rays, deflected in a magnetic field, was made to register its deflection on a photographic plate both after passage through a thickness of aluminium foil and when the foil was removed, and he obtained the same result as in Rutherford's experiments, that the beam is more easily deviated after passage through aluminium foil, and therefore suffers retardation of velocity in its passage through matter. The earlier view that there was an increase in the radius of curvature along the trajectory is shown by the new experiments to have been erroneous, and the traces conform to a circular trajectory.

Rutherford⁶ reproduces photographs of a very striking character, showing clearly the displacement of the trace in the direction of greater deviability when the α -rays are caused to pass through 0.003 cm. of aluminium foil, using the homogeneous α -radiation from

¹ *Ann. Report*, 1905, 302.

² *Compt. rend.*, 1905, 141, 485.

³ *Phil. Mag.*, 1906, [vi], 11, 166.

⁴ *Ibid.*, 627.

⁵ *Compt. rend.*, 1906, 142, 365; *Phil. Mag.*, 1906, [vi], 11, 722; *Phys. Zeit.*, 1906, 7, 177.

⁶ *Loc. cit.*

radium *C*, whilst in another photograph the broad diffuse trace obtained by using a thick layer of a radium salt, emitting several types of α -rays travelling with different velocities, is contrasted with the result when a homogeneous source of α -rays is employed. In addition, the photographs establish a slight but distinct *scattering* of the beam consequent upon its passage through matter. Thus in one photograph the impressions produced by the rays of radium *C*, (1) in a vacuum, (2) after passage through air, are contrasted, and it is clear that not only can the rays be deviated to a greater extent, but the trace is broader and less well defined in the second case than in the first. This is an important result, as Bragg and Kleeman¹ had shown that if any such scattering in passage through matter occurs it can only be small, and is sharply to be distinguished from the very marked scattering that is shown by the β -rays.

Rutherford,² in a paper entitled "The Retardation of the α -Particle in passing through Matter," gives some data differing somewhat from the preliminary measurements already given.³ It will be recalled that there exists a certain sharply defined "critical velocity" at which all action of the α -ray abruptly ceases, so that even although it is moving at great speed it produces no ionising, photographic, or fluorescent action. This critical velocity is now given as $0.43 V$, where V indicates in all cases the initial velocity at which the α -particle of radium *C*, the fastest of those from radium, is expelled. It was found when successive thicknesses of aluminium foil were placed over the source of α -rays that each layer caused a reduction of velocity by an amount greater than the last, but the simple law was established that the diminution of the kinetic energy, or the square of the velocity, of the α -particle was the same amount for each layer of foil added. If the kinetic energy is plotted against the thickness of matter traversed, a straight line is obtained which if produced cuts the axis of zero energy at a point represented by 8.31 centimetres of air, that is, 1.25 cm. beyond the critical distance at which the rays cease abruptly to ionise. This has proved a very useful result, although it may be said at once that we have at present no knowledge of what becomes of the α -particle after it has passed through its critical distance. Bronson⁴ made a search for any small ionisation by the α -rays beyond their critical distance, but with negative results. The drain on the energy of the α -particle on account of ionisation ceases after the critical distance is passed, so that unless other actions, of which we have at present no knowledge, occur, there may be no cause acting to retard the velocity further once the critical velocity is reached. J. J. Thomson⁵ has

¹ *Ann. Report*, 1906, 297.

² *Phil. Mag.*, 1906, [vi], 12, 134.

³ *Ann. Report*, 1906, 300.

⁴ *Phil. Mag.*, 1906, [vi], 11, 806.

⁵ *Proc. Camb. Phil. Soc.*, 1906, 13, 212.

suggested that the most probable cause of the loss of ionising power by the α -particle is that below the critical velocity it retains an electron and becomes an uncharged atom.¹

If r is the range of any α -particle in air, its energy is proportional to $r+1.25$ and its velocity to $\sqrt{r+1.25}$. The ratio of the velocity of two particles with ranges r_1 and r_2 respectively is therefore $\sqrt{\frac{r_1+1.25}{r_2+1.25}}$. In this way Rutherford has calculated, in terms of that of radium C as V , the velocities of each of the α -particles expelled by radium and its products, using the ionisation ranges as determined by Bragg. These are: Radium, 0.750 V ; emanation, 0.814 V (see p. 344); radium A , 0.858 V ; radium F (polonium), 0.787 V . These results agree closely with the direct measurements about to be considered. From the scattering of the α -rays in passage through matter it was deduced that some of the rays must suffer a deflection of at least 2° from their course, which is equivalent to the effect of an electric field of a hundred million volts per centimetre (compare preceding footnote).

After four years' efforts, Rutherford has now obtained satisfactory measurements of the electrostatic as well as of the electromagnetic deviations suffered by the α -particle.² The former gives the value mv^2/e and the latter the value mv/e , so that from the combined results the velocity v and the ratio e/m of the charge to the mass of the particle can be deduced. The α -rays of radium C , from an uncovered wire made active by exposure to the emanation, were taken as the standard, and the values in other cases deduced by comparison with this standard. The initial velocity of the α -rays from radium C , designated by V previously, is given as 2.06×10^9 cm. per second, and the ratio e/m as 5.07×10^3 . These values are both somewhat lower than those previously given from more or less indirect data, and for the future they must be taken as the most trustworthy determinations of these important and difficultly-determined constants.

Rutherford next proceeded to examine whether the ratio e/m is the same for all α -particles, and whether it is altered by passage of the α -particle through matter. Direct determinations of the electrostatic and magnetic deviation of the α -particle of radium C after passing through various thicknesses of matter showed that the ratio e/m is constant within the limit of experimental error. Similar direct deter-

¹ The assumption seems to be made here that only electrical forces are acting in the collision of the radiant α -particle with the molecules of obstructing matter. But this view presupposes that an uncharged radiant atom would neither ionise nor be retarded or deviated in its passage through matter, an assumption which is far from proved.

² *Phil. Mag.*, 1906, [vi], 12, 348.

minations were also made of the α -particles of radium *A*, radium *F*, and actinium *B*, and, in conjunction with Dr. Hahn,¹ of the α -rays from the excited activity of thorium (thorium *B* and thorium *C*, p. 342). An independent determination in the case of radium *F'* or polonium has been carried out by Huff² in continuation of the work of A. Stanley Mackenzie. The general result goes to show that the ratio e/m is the same for all the α -particles within the limits of experimental error.

Lastly, the evidence is considered by Rutherford as to the connexion between the α -particle and the atom of helium. All the radio-elements expel α -particles which are identical in all respects save initial velocity of expulsion, and it is pointed out that whatever its nature the α -particle must be a fundamental constituent of the atoms of all the radio-elements. Now the new value for e/m , 5.07×10^3 , is almost exactly one-half that of the hydrogen ion in electrolysis (10^4), and since the atomic weight of helium is accepted as 4, the helium atom, if it carried the single ionic charge carried by the hydrogen ion, would have the value 2.5×10^3 for the ratio e/m , or one-half that of the α -particle. Several possibilities are discussed by Rutherford, and two may be here considered. The α -particle may be a helium atom with twice the ionic charge, or it may be one-half the chemical atom carrying a single charge. The first alternative is that favoured by Rutherford. Another possibility not discussed is that there is a flaw in the reasoning which has led in the case of the inert gases to the density being doubled to give the atomic weight. Beyond the general evidence already discussed³ in favour of regarding helium as a general product of radioactive matter, and therefore that the α -particle is or becomes an atom of helium, there is very little actual evidence at the present time on which to base a conclusion. A large number of calculations in radioactivity are based on the hitherto unquestioned assumption that the α -particle carries the single ionic charge, and if that assumption is abandoned, not only are the values of these calculations affected, but in addition much of the foundation on which the atomic theory of electricity has been based is weakened, for the existence of multiple charges, not confined to two units only, may be postulated in many other cases. Until the question is settled, doubt is thrown upon most of the calculated constants in radioactivity, for example, the number of α -particles expelled from a known weight of a radioactive substance in unit time, the periods of average life of the parent elements, the quantity of the disintegration products associated with the parent in state of radioactive equilibrium, &c., which must be either doubled or halved on the view that the α -particle carries two ionic charges. Rutherford calculates, on the latter assumption, the period

¹ *Phil. Mag.*, 1906, [vi], 12, 371.

² *Proc. Roy. Soc.*, 1906, 78 A, 77.

³ *Ann. Report*, 1905, 303.

of past time required for the generation of the helium in two minerals, thorianite and fergusonite, and arrives in each case at about the same result, namely 400 million years, which brings vividly into prominence the slowness of radioactive change and the extraordinary delicacy of our present means of investigation.

α -Ray Ionisation.—The phenomenon of “initial recombination” discovered by Bragg and Kleeman working with the α -rays of radium¹ has been the subject of a further investigation by Kleeman,² who has made the important discovery that the effect appears to be confined to ionisation produced by the α -rays alone. Gases ionised by the action of X-rays, β -rays, and γ -rays do not show the effect, and this is attributed to the relatively low velocity of the α -particle, and the consequently less violent character of the separation of the charged ions from the neutral atom in this case. The view that in α -ray ionisation the electron detached from the atom ionised travels at a low speed, and so is more readily dragged back into, or recombines with, the parent atom by the electric field existing between them, after the α -particle has passed, is supported by the fact that the α -rays produce no secondary radiation where they impinge, whereas the other radiations give rise to strong secondary radiation known to consist of electrons moving with great velocity. It was found that the effect of the initial recombination was the greater the lower the velocity of the α -particle.

Bragg³ has attacked an important problem in the nature of ionisation, namely, the determination of the relative total number of ions produced by the α -rays in various gases. Several distinct factors have to be considered separately in ionisation by α -rays. The ionisation per unit length of path of the α -particle, or the specific ionisation, increases with the distance traversed up to the critical velocity, and therefore with diminishing velocity and energy the α -particle becomes a more efficient ioniser right up to the point at which it ceases to ionise. Combining with his earlier results the direct measurements of the velocity by Rutherford, it appears that the ionisation increases inversely as the velocity. Since we have seen that the energy lost by the α -particle in traversing unit length of path (in aluminium) is constant, it may be inferred that the energy required to produce an ion cannot be constant, but must be greater at the beginning than at the end of the course of the α -particle.

The range of the α -particle in any gas, or conversely the “stopping power” of the gas, is easily measured to very great accuracy, and is simply proportional to the number of molecules in the layer of gas,

¹ *Ann. Report*, 1905, 298.

² *Phil. Mag.*, 1906, [vi], 12, 273.

³ *Trans. Roy. Soc. S. Australia* 1906, 30, two papers; *Phil. Mag.*, 1906, [vi], 11, 617.; 1907, [vi], 13, 333.

and with this reservation is not affected by pressure and temperature, and is independent of the chemical nature of the gas. It is a strictly colligative or additive property depending only on the number and nature of the individual atoms. The stopping power of different atoms is very nearly proportional to the square root of the atomic weight, but there is a slight systematic departure from this law, the value being more accurately expressed by $a\sqrt{w} + bw$ than by $a\sqrt{w}$ simply, where a and b are two constants the same for all the elements. Bragg considers stopping power more nearly a purely additive property of the atom than any other save mass. The proportionality of stopping power to the atomic square root is an effect quite apart from its additive nature, and the divergence from exactness is only marked for light atoms below 30, an effect which is curiously similar to the case of the atomic heats.

The total ionisation produced by the α -particle in different gases is a very difficult quantity to measure accurately, and, as is evident from the papers, a great deal of experimental skill has been spent on this part of the problem. The method employed is to determine the specific ionisation at some defined point on the curve connecting ionisation with distance from the source, and that point to which the rays from radium A (the second most penetrating type) just fail to penetrate was selected. The product of this quantity into the range of the α -particle in the gas in question gives a measure of the desired total ionisation, by means of which different gases can be compared together. Initial recombination was carefully guarded against by the use of extremely high voltages, which previous work had shown were necessary in many of the complex gases to produce complete saturation. It was definitely proved that the total ionisation in different gases was very different from that in air, being in the majority of gases tried about one-third higher. Thus the value in the case of carbon disulphide is 1.37 times air, and this is one of the highest determined. Then in order come pentane, methyl iodide, ethyl ether, ethyl chloride, carbon tetrachloride, chloroform, ethyl iodide, ethylene, and lastly acetylene with the value 1.26. The simple gases carbon dioxide, nitrous oxide, and hydrogen are very similar to air. The specific molecular ionisation, or the relative ionisation produced in the molecule by the passage of an α -particle of defined speed, obtained from these data is shown by Bragg to be closely related to other physical constants, such as molecular volume, molecular refractive power, and more closely still to Sutherland's molecular-volume constant B . Thus, although range is strictly additive, capacity for being ionised is a constitutive property of the molecule, and the energy required to produce an ion is not constant. This shows that in the special case of ionisation by radiant

atoms or α -particles, the act of ionisation is not entirely a sub-atomic process whatever it may be in other cases.¹

Initial recombination is an effect which varies greatly for different gases and, as Kleeman has also shown, with the speed of the α -particle. There does not appear to be any evidence against the view that a molecule which has already lost one ion or electron is any the less likely to be again ionised, or, in other words, there seems no evidence against the existence of gaseous ions with multiple charges, as concluded by Rutherford in the case of the α -particle itself.

In the same paper, Bragg draws attention to a suggestive fact also commented on by Rutherford independently.² The number of ions made in a day by radium would occupy the same volume approximately as the hydrogen and oxygen generated in the same time by the radium in aqueous solution. In other words, if the saturation current capable of passing through a gas ionised by radium were passed also through a water voltameter in series, the gas generated in the voltameter would be nearly equal in volume to the gas generated by the same radium in aqueous solution. The question naturally arises whether the hydrogen and oxygen liberated are not actually the ions formed by the α -rays in passing through liquid water. And this at once leads to fundamental questions affecting the ionisation of liquids which cannot at present be answered. Thus the whole subject of the nature of ionisation is in a very interesting state, and great advances are foreshadowed, which may have a bearing on chemistry and electrochemical problems. In particular, it is noteworthy that two of the main ideas, which served almost as a scaffolding on which the existing ionisation theory of gases was largely based during its development, namely, the confident assumption that the charge carried by the gas ion was always the same and equal to the single atomic charge, and secondly that the energy required to produce a pair of ions was independent of the nature of the gas, appear (in the light of fuller knowledge) not to have been warranted.

Ionisation ranges of α -rays.—Steady progress has been made in the determination of the ionisation ranges of the α -rays of other substances than radium by numerous investigators, following the methods of Bragg and Kleeman. McClung³ investigated in this way the α -radiation of radium *C* by itself and found it homogeneous, as was to be expected from the original curves of Bragg and Kleeman. The same homogeneity has been found independently by many investigators in the case of the radiation from polonium or radium *F*. Kleeman⁴ found a

¹ Compare *Ann. Report*, 1905, 298.

² *Radioactive Transformations*, 252. (Constable & Co., 1906.)

³ *Phil. Mag.*, 1906, [vi], 11, 131.

⁴ *Ibid.*, 12, 273.

range in air of 3.8 cm. at 77.34 cm. of mercury pressure. Levin¹ found 3.86 cm. at 76 cm., and Kučera and Mašek 4.1 cm. at 73.3 cm. The results of the latter investigators² are the most complete. They showed that the range of the rays is not affected by the decay of the activity of the polonium with time; the number of rays expelled grows less, but the character of the individual particle expelled remains the same. Absorption of the rays of polonium by metal films and gases confirmed the square-root law of Bragg and Kleeman. Lastly, they state that it is not possible to observe any secondary radiation from the α -rays where they impinge, and the effects previously ascribed to this are probably due to the scattering of the original beam, which increases with the atomic weight of the metal acted on. This agrees with the conclusion of Kleeman (p. 338). On the other hand, Edgar Meyer,³ investigating the nature of the absorption of the α -rays of polonium by metals, concludes that neither secondary radiation nor scattering are necessary to explain the results. The main fact in question is that if two screens of different metals, as aluminium and tin, are used to absorb the rays, the extent of absorption is different according to the order in which the screens are traversed by the rays.⁴ It would appear that all that is necessary to explain these and similar results is to suppose that the absorption like ionisation in gases increases as the velocity of the α -particle decreases. On this view, the effect of superimposing various screens in different ways can be calculated, and the results given agree closely with experiment. Further discussion must be held over.

In apparent contradiction to the above conclusions that the α -rays produce no secondary radiation by impact is a research of W. H. Logeman,⁵ who has proved in a very neat manner the existence of a secondary radiation from a metal plate in a vacuum bombarded by the α -rays of polonium. The contradiction is but apparent, for the secondary rays in question are so feeble in penetrating power that they could only be observed by working in a vacuum, and consist of the slow-moving electrons or δ -rays discovered by J. J. Thomson. With no electric field acting, a plate of polonium gives out to an opposed plate more - than + electricity, but by the application of an electric field in the right direction the emission of negative electricity from the polonium plate can be suppressed, so that the + emission predominates. If, however, a suitable magnetic field is employed to deviate the negative charges and to return them to their origin, the + emission is only one-fifth of that when the electric field is employed. The explanation is that the plate bombarded gives out slow-moving

¹ *Phys. Zeit.*, 1906, **7**, 519; *Amer. J. Sci.*, 1906, **22**, 8.

² *Phys. Zeit.*, 1906, **7**, 337, 631 and 650.

³ *Ibid.*, 917.

⁴ Mme. Curie, *Thesis* reprinted from the *Chemical News*, p. 56.

⁵ *Proc. Roy. Soc.*, 1906, **78 A**, 212.

negative charges no less than the polonium plate, and these also are readily returned to their origin by the magnetic field. The electric field, on the other hand, which suppresses the negative charges from the polonium, carries those from the bombarded plate to the polonium plate, and the effect is added to the positive current conveyed by the α -particles from the polonium to the bombarded plate. The positive current then appears to be much greater than when a magnetic field is acting.

Returning to the subject of ionisation ranges, Hahn¹ has applied the method with fruitful and novel results to the α -rays of actinium and thorium. This has been rendered possible by the separation from these elements of intensely active new disintegration products, radioactinium and radiothorium, some account of which follows later (p. 363). Only very intensely active preparations are suitable for the determination of ionisation ranges, and the extension of the results to thorium, as also the case of Rutherford and Hahn's measurement of the constants of the α -rays from this element already described, exemplifies the very valuable results that have followed the separation of radiothorium. Both radiothorium and radioactinium are considered to be the *first* product of the parent element, the initial change of which is in each case rayless, so that these preparations exhibit in intensified degree *the whole* of the characteristic radioactivity of the parent elements. The excited activity of thorium was first investigated. Hitherto it has been supposed that the rays in this case come solely from thorium *B*, as thorium *A*, the first product deposited from the thorium emanation, undergoes an apparently rayless change (see, however, p. 348). It was at once seen that the curve connecting ionisation with distance was not due to a homogeneous type of α -radiation, but to two types of different ranges superimposed. The ranges in air were 8.6 cm. and 5.0 cm. Sufficient grounds are furnished in the paper for the conclusion that the radiation of thorium *B* is derived from two successive products, called thorium *B* and thorium *C*, both of which give out α -rays on disintegration, but it is not yet possible to say which change gives the more penetrating and which the less penetrating type. From analogy to radium it is provisionally concluded that the thorium *C* gives the more penetrating type and also the β - and γ -rays. According to the evidence, the change of thorium *B* into thorium *C* must be extremely rapid, for the two types occur together in all circumstances in unchanged relative amount, and for this reason no actual separation has been effected. The new type of α -rays here disclosed must not be confounded with yet another new type found this year from thorium *A* by von Lerch (p. 348).

The curve in the case of the α -radiation of radiothorium itself, freed

¹ *Phil. Mag.*, 1906, [vi], 11, 792; 12, 82.

from succeeding products, proved to be simple, the rays having a range of approximately 3.9 cm. The curve for thorium *X* freed from the later products disclosed also a homogeneous α -radiation of range 5.7 cm. The range of the rays from the thorium emanation was estimated by a special scintillation method to be about 5.5 cm. Thus the whole of the ranges of the five types of α -rays emitted by thorium have been determined, and it is interesting that the range is on the average higher and the velocity therefore greater than in the case of radium. Indeed, the α -particle of range 8.6 cm. from thorium *C* is the fastest moving α -particle known. A beautiful photograph showing the lesser deviation suffered by this particle in comparison with that from radium *C*, the swiftest particle from radium, is to be found in Rutherford and Hahn's paper on the mass and velocity of the α -particles from thorium already referred to. On the clear view afforded by the disintegration theory, it is of course a matter of no comment that a feebly active body like thorium should emit an α -particle with greater velocity and energy than in the case of an intensely active body like radium, but no more striking example could be deduced of the independence of the rate of atomic disintegration, not only on its external environment, but also on the quantity of internal energy liberated in the process.

Some observations of Lise Meitner¹ on the α -rays of thorium *B* resulted in the confirmation of the square-root law of absorption of Bragg. In the case of the β -rays the absorption does not follow the square-root law, but increases with, although slower than, the specific gravity of the metal.

For actinium, Hahn² gives the following ranges for the four types of α -radiation: radio-actinium, 4.8 cm.; actinium *X*, 6.55 cm.; actinium emanation, 5.8 cm.; actinium *B*, 5.50 cm. In the relative magnitude of the ranges of the rays of the successive products the actinium series bears a close resemblance to that of thorium, a resemblance which is extending itself to all the radioactive properties of the two substances. The various α -rays from actinium are the most nearly alike in range, those from thorium exhibit the greatest diversity, whilst those from radium occupy an intermediate position. The α -radiation from the excited activity of actinium (actinium *B*), unlike that from thorium, is completely homogeneous.

The researches of H. Willy Schmidt,³ remarkable in many directions discussed later, have resulted incidentally in settling the question left open from Bragg and Kleeman's work⁴ of the respective ranges of the α -rays from radium *A* and the radium emanation. Schmidt has

¹ *Phys. Zeit.*, 1906, 7, 588.

² *Phil. Mag.*, 1906, [vi], 12, 244.

³ *Phys. Zeit.*, 1905, 6, 897; 1906, 7, 764; *Ann. Physik.*, 1906, [iv], 21, 609.

⁴ *Ann. Report* 1905, 296.

shown that the less penetrating of the two types of α -radiation present in the radiation from the active deposit immediately after its formation from the radium emanation, and which is due to radium *A*, has a range greater than 4.5 cm. and less than 5.1 cm., so that the range of 4.83 cm. measured by Bragg must be ascribed to the rays from radium *A*, and that of 4.23 cm. to the rays from the radium emanation.

For use in cases of feebly radioactive bodies where a direct determination of the range of the α -radiation is impossible, Bragg¹ has derived an indirect method which he has applied to the determination of the ranges of the α -rays from uranium and thorium. Bragg obtains mathematically an expression connecting ionisation current due to α -rays, from layers of radioactive matter of various depths covered with uniform sheets of metal of various thickness and known stopping power, with the range of the α -ray in question, in such a way that the range can be deduced from measurement of the ionisation current under various conditions. In this way it is shown that the initial α -ray expelled from both thorium and uranium has the same range as that of the initial α -ray expelled from radium, namely, about 3.5 cm. This is in fair agreement with the direct measurement of Hahn for thorium (radiothorium), which gave 3.9 cm. (p. 342). From the relative ionisation produced from similar quantities of uranium and thorium preparations, and the number of α -ray changes in each case contributing to the activity, Bragg has deduced the relative rates of change of these two elements to be in the ratio of 5 to 1. Uranium and thorium are of very similar α -activity, but since there are five successive changes contributing α -rays in thorium and only one in uranium, the uranium must be disintegrating much the more rapidly. The actual ratio of Bragg is, however, vitiated, as Rutherford has pointed out, by the subsequent work of Dadourian and Boltwood (p. 362), who has shown that commercial thorium preparations do not contain their full amount of radiothorium, about half being apparently separated during the process of manufacture. To get the true ratio, which is probably about 5 to 2, the measurements must be repeated with some thorium mineral, such as thorianite, containing a known percentage of thorium in equilibrium with its disintegration products.

Positive Charge carried by the α -Particle.—The difficult question as to whether the α -particle is charged at the moment of its expulsion from the parent atom² has this year been experimentally attacked by Ewers³ and Soddy.⁴ Ewers investigated the α -rays of polonium in the highest vacuum he could produce, and obtained no difference in the value of the charge carried by the α -rays on account of the high vacuum. He concluded against the hypothesis that the α -particle was uncharged

¹ *Phil. Mag.*, 1906, [vi], 11, 754.

² Compare *Ann. Report*, 1905, 302.

³ *Phys. Zeit.*, 1906, 7, 148.

⁴ *Nature*, Aug. 2nd, 1906, p. 316.

at the moment of its expulsion from the parent atom. He also measured the constants of the slow-velocity electrons (δ -rays) accompanying the α -radiation, and found for e/m 1.48×10^7 and for v 3.25×10^8 , which, however, are not in agreement with the experiments of Logeman (p. 341). It has been pointed out by Bragg¹ and Soddy² that the experiments of Ewers do not suffice to answer the question as to the initial state of the α -particle on expulsion, for in his experiments the α -particles must first pass through the thickness of the radioactive layer of polonium, and must, therefore, become charged before emerging into the vacuum. The conditions to be realised are, according to Soddy, not only a vacuum so high that no gas molecule is encountered by the α -particle in its path, but also a layer of radioactive matter as the source of α -rays, not exceeding one molecule in thickness. This was attempted experimentally by using radium *C* as the source of α -rays, the deposit being produced inside, and confined within a certain length of, thermometer tubing of the smallest possible bore, from one of the open ends of which a narrow pencil of α -rays emerged. Under the action of a magnetic field the rays are readily deviated, and none escapes the narrow tube. After many failures, it was found in three consecutive experiments that a magnetic field which completely deviated the beam in a low vacuum no longer affected it in the highest possible vacuum, and it was concluded that the α -particle was uncharged on expulsion. Only a preliminary account of this work has so far appeared.

The Disintegration Series radium *A*, radium *B*, radium *C*.—This series has hitherto presented some anomalies and unexplained divergences from the requirements of the simple theory, which have received during the year exhaustive and critical examination, resulting in the complete vindication of the theory in its original form. Rutherford concluded³ that his experimental results would agree more closely with theory if radium *A* and radium *B* were regarded as simultaneous rather than as successive products of the radium emanation, but that further work was required before so fundamental a conclusion could be accepted. A similar idea has been proposed by him⁴ to account for the position of actinium in the uranium-radium series, which is also anomalous. However, new results have, so far at least as the radium series is concerned, dispensed with the necessity of the above assumption. The conclusion of Bronson⁵ that radium *B* has a longer period of change than radium *C*, instead of the contrary as previously assumed, and that both periods must be reduced, has also been arrived at independently by H. W. Schmidt

¹ *Phys. Zeit.*, 1906, **7**, 452.

² *Loc. cit.*

³ Compare *Radioactive Transformations*, p. 115.

⁴ *Ibid.*, p. 177.

⁵ *Phil. Mag.*, 1906, [vi], **11**, 143; *Ann. Report*, 1905, 307.

and by von Lerch. The latter¹ arrived at his conclusions by the electrochemical separation of the two products radium *B* and radium *C*, the former of which has been regarded as rayless, but as producing radium *C*, which then gives all three kinds of rays. Radium *C* behaves as electrochemically "nobler" than radium *B*, and by immersing a copper or nickel plate in the solution of the active deposit, or by electrolysis with small current density using a polished platinum cathode, only the radium *C* is deposited. In the same way, thorium *B* (+thorium *C*) is separated from thorium *A*, hitherto regarded as rayless.² If barium is precipitated as sulphate in the solution, the radium *C* remains in solution while the radium *B* is carried down with the precipitate. Copper precipitated with caustic potash leaves some of the radium *B* in solution, the remainder, together with the radium *C*, being precipitated. The radium *C*, whether separated as in Bronson's methods by volatilisation of the radium *B*, or by the new methods of von Lerch, has the quicker period.

H. W. Schmidt,³ in addition to showing that the decay curves could be better explained by supposing that radium *C* possessed the quicker period, has shown that the change of radium *B* into radium *C* is not altogether rayless, as previously assumed, but that β -rays of a type unusually feeble in penetrating power are emitted, and with these two additions the experimental results agree perfectly with the theory without further assumptions. The same discovery of the emission of β -rays from radium *B* has been made independently by W. Duane⁴ and by Gruner,⁵ the latter in a mathematical contribution to the theory of radioactive change, from a study of the experimental results of Curie and Danne. Schmidt investigated the decay curves of the active deposit on a wire, immediately after short exposure to the radium emanation, through metal screens of successively increasing thickness. 0.03 mm. of aluminium cuts off all the α -rays from radium *A*, and the decay curve, instead of showing the sharp initial decay characteristic of the change of radium *A*, rises to a maximum steadily in thirty minutes. With increasing thickness of aluminium the maximum is reached sooner, and with 0.068 mm. in eleven minutes. Screens, successively added, of 0.1, 0.2, and 0.4 mm. caused the period of maximum again to increase until it reached thirty-five minutes. The only explanation is that radium *B* gives out rays somewhat more penetrating than α -rays and less penetrating than the common β -rays.

In a further examination, the methods of von Lerch in separating radium *B* and radium *C* were employed, and it was found that the β -rays of radium *B* could be deviated by a magnetic field, and more

¹ *Wien. Sitzungsber.*, 1906, **115**, Abt. IIa, 197; *Ann. Physik.*, 1906, [iv], **20**, 345.

² *Ibid.*, March, 1905.

³ *Loc. cit.*, p. 343.

⁴ *Science*, 1906, **24**, 48.

⁵ *Ann. Physik.*, 1906, [iv], **19**, 189.

readily, so that they must travel at a lower velocity than those of radium *C*. Duane has shown that they carry negative charges. The periods¹ of the three products may be taken as follows: radium *A*, three minutes; radium *B*, twenty-six minutes; radium *C*, nineteen minutes; and the theoretical curves calculated from these periods now agree far better with the experimental than if it is supposed that radium *A* and radium *B* are simultaneous products.

Bronson,² in a special research, examined the radiation of radium *B* to see if α -rays, possibly of very slight penetrating power, were also given out, but with a negative result.

Another question remains for consideration in connexion with this disintegration series. Curie and Danne had explained their experimental results originally on the view that the rate of transformation in this series is affected by high temperature, and the effect of submitting the active deposit to a high temperature has been examined both by Bronson and Makower with contradictory results. The former³ maintains that there is no alteration of the rate of change. Wires made active in the radium emanation were afterwards sealed into tubes of hard glass, so that none of the radioactive matter could escape by volatilisation, and were heated, it is stated, up to temperatures of at least 1100°. It is difficult, however, to believe that such high temperatures can be attained with glass tubes. Makower,⁴ working at much higher temperatures in vessels of sealed quartz, investigated the effect of heating on the external radiation from the excited activity inside the vessel. The rays in question are the β - and γ -rays derived from radium *C* and not from the emanation. The activity measured immediately after the tube had been heated for fifteen minutes to a temperature between the melting points of platinum and of nickel was found to have fallen about 15 per cent., but in the course of an hour recovered its original value. This was repeated five times for the same tube with similar results, and in a second experiment at lower temperatures (1000° to 1200°) it was found that while heating for ten minutes had little effect, heating for one hour produced a temporary lowering of activity of from 4 to 9 per cent., while longer heating produced no further effect. In a further paper to the Royal Society just published, Bronson⁵ has maintained his original conclusion, and states that there is no alteration in the constants between -180° and 1600°, so that the question therefore remains unsettled.

¹ By "period" used as above without further qualification is now commonly understood the period of half-transformation. Multiplying this by 1.45 gives the "average life" which is the time required for the quantity to be reduced to e^{-1} (0.368) of the initial. The reciprocal of the average life is the "radioactive constant" λ .

² *Phil. Mag.*, 1906, [vi], 11, 810.

⁴ *Proc. Roy. Soc.*, 1906, 77 A, 241.

³ *Ibid.*, 142.

⁵ *Ibid.*, 1907, 78, A, 494.

Other α -Radiations previously overlooked.—Closely connected with the preceding results are two researches which have resulted in the discovery of radiations previously overlooked in other disintegrations. Von Lerch¹ has concluded that thorium *A*, hitherto regarded as rayless, emits a small amount of ionising radiation, in part less penetrating, but chiefly more penetrating in character than the α -rays emitted by thorium *B* (+ thorium *C*). Thorium *B* was separated electrochemically from thorium *A*, and the radiation of the former compared with that of the unseparated activity using various thicknesses of absorbing screens. The close agreement between the decay curves and theory on the earlier assumption that the change of thorium *A* is rayless, shows that the amount of radiation from this body must be relatively small.

Moore and Schlundt,² in an investigation of new methods of separation of uranium *X* from uranium, have made the observation that the radiation of uranium *X* is not entirely due to β -rays, as before thought, but that there is a small amount of a feebly penetrating radiation also, which they ascribe without sufficient proof to α -rays. Hitherto, although it has been noticed that uranium *X* has a feeble non-penetrating radiation, this has been attributed to a trace of uranium not completely separated. Moore and Schlundt, however, show that this cannot be the case, for the two types of radiation both decay, and at the same rate. A more thorough examination of this radiation is much to be desired, for the results of the authors give no clue to the real nature of the radiation, whether it is an α -radiation as they assume, or a feebly penetrating β -radiation of the type given by radium *B*. The new methods of separation referred to consist in dissolving uranyl nitrate in various solvents, acetone, various alcohols, methyl and ethyl acetate, &c., stirring in a little freshly precipitated ferric hydroxide, and filtering. The filtrate containing the uranium is found to be quite free from uranium *X*, which remains with the precipitate. Another case of a feeble radiation previously overlooked is considered under actinium (p. 363).

β -Rays.—Important advances have also been made in our knowledge of the β -rays, and a beginning, perhaps, made in a theory of the mechanism of their absorption by matter, which is so markedly different in nature from that shown by Bragg for the α -rays.

It has always been suspected without actual proof that in thorium, as in radium, the β -rays result only in the last change, but until now the difficulty of separating thorium *X* from the later products, giving β -rays, has prevented a definite answer to the question. Levin³ has investigated from this point of view both thorium and actinium,

¹ *Phys. Zeit.*, 1906, 7, 913.

² *Phil. Mag.*, 1906, [vi], 12, 393

³ *Ibid.*, 177.

and has concluded that the only members of the series producing β -rays are in each case the last, thorium *B* (+ thorium *C*) and actinium *B*. Thorium *X* carefully separated from later products of change possesses only two or three per cent. of the β -activity ultimately attained, and actinium *X* is similar.

A very complete examination of the absorption of the β -rays of uranium has been made by J. A. Crowther.¹ As Rutherford has shown, this radiation is fairly homogeneous, and absorbed according to an exponential law, $I/I_0 = e^{-\lambda d}$, where I is the intensity of the radiation, initially of intensity I_0 , after passage through a thickness d of material. λ is the coefficient of absorption. This coefficient is not proportional to the density (ρ), and λ/ρ varies from 5.7 for glass, mica, wood, iron, and aluminium to 13.2 for tin, whereas Lenard found for the cathode rays of the Crookes tube that the absorption was strictly proportional to density (Lenard's density law). Godlewski has shown that the β -rays of actinium are also homogeneous and absorbed exponentially, while here the variations from the density law are smaller. Crowther has determined λ/ρ for thirty elements, and finds that the latter arrange themselves in groups according to the groups of the periodic table when the value of λ/ρ is plotted against the atomic weight. In compounds the absorption is strictly additive, and the secondary radiation set up by the β -rays of uranium is much less than that produced by the β -rays of radium.

H. W. Schmidt² has investigated the β -radiation of radium (derived from radium *B* and radium *C*), and made the remarkable observation that within certain screen thicknesses the absorption of both types proceeds according to an exponential law. In this way he analysed the β -radiation into five homogeneous types, three derived from radium *B* and two from radium *C*. For the former the respective thicknesses of aluminium required for half absorption are 0.0078, 0.087, and 0.53 mm., for the latter 0.131 and 0.53 mm. He points out that it is doubtful if such an analysis can have a real physical meaning, but if so, it seems to open the way to a clearer view of the mechanism of absorption. It seems possible, if the absorption of β -rays follows an exponential law, that the β -particle passes through the atoms of matter completely unchecked until it is suddenly and completely stopped. This view accords with Kaufmann's work that the velocity of the β -particles which escape an absorbing screen are not retarded during their passage through the screen, and with Kleeman's observation that ionisation produced by β -rays after passage through a thick aluminium plate shows little tendency to initial recombination.

Secondary Radiation of β - Rays.—This view accounts well also for the

¹ *Phil. Mag.*, 1906, [vi], **12**, 379.

² *Phys. Zeit.*, 1906, **7**, 764; *Ann. Physik.*, 1906, [iv], **21**, 609.

fact observed by McClelland, and recently examined by S. J. Allen,¹ that the velocity and the penetrating power of the electrons constituting the secondary radiation set up by impact of the β -rays is not greatly, if at all, less than for the primary rays themselves, for the "stopping" of the primary rays may well consist in their being turned through a large arc, as a comet at perihelion, to reappear as secondary rays at the bombarded surface. S. J. Allen repeated and confirmed by an electrical method the work of Kaufmann, and found also that the ratio e/m of the secondary radiation, like that of the primary, increases with the velocity of the secondary ray. McClelland² and McClelland and Hackett,³ in continuation of their investigations on secondary radiation, found that the energy of the secondary radiation from a plate of lead, for example, was equal to one half of the energy of the primary rays. The ratio diminished with the atomic weight of the metal, being lowest for carbon and next lowest, but still above 20 per cent., for sodium, aluminium, and magnesium. The secondary radiation of compounds is an additive function of the component elements, and can be calculated from the radiating power of the constituents. The important influence of secondary radiation on the apparent coefficient of absorption of the primary rays is pointed out, and it is stated that owing to successive generation of fresh β -particles as secondary rays the apparent distance penetrated by the primary rays is much increased.

K. Seigl⁴ showed that the secondary radiation produced on impact by the β -rays of radium is capable of exciting strong fluorescence in barium platinocyanide. It was weakest for aluminium and strongest for lead, increasing with the atomic weight of the metal, as McClelland has shown. Using tinfoil, it was found that the effect increased with successive numbers of layers of foil up to 50 layers.

The Electronic Theory of Matter.—It may be stated without fear of contradiction that the theory that the atom is made up entirely or to any substantial extent of electrons is now generally regarded as being very much open to question. From spectroscopic and other evidence it is certain that electrons are universal constituents of atoms, but for the further very sweeping deduction that the atoms are composed of electrons there never has been much positive evidence in the past, whilst against the view some definite experimental evidence can now be urged. It is interesting to note that Prof. J. J. Thomson, to whom the electronic theory of matter is largely due, has himself this year brought forward considerations which have practically made the theory untenable. The view that the β -ray electrons do not in their passage through matter diminish continuously in speed, but proceed more or less unaffected

¹ *Phys. Review*, 1906, **22**, 375.

² *Trans. Roy. Dubl. Soc.*, 1906, ii, **9**, 9.

³ *Ibid.*, p. 27.

⁴ *Phys. Zeit.*, 1906, **7**, 106.

until they are suddenly stopped or turned through a large angle to reappear as secondary radiation, bears upon the present question. Considering the enormous number of atoms a β -ray electron can penetrate without being greatly affected, and the certainty that the approach of the radiant electron to an electron in an atom must result in deviation or loss of velocity of the former, it becomes extremely difficult to believe in the reality of the view that the atom is substantially constituted of swarms of electrons in regular motion. The penetrating power of the β -ray electron was one of three methods developed by J. J. Thomson¹ to determine the number of electrons in an atom, each of which led to the result, the importance of which cannot be overestimated, that the number of electrons in any atom is of the same order as, and probably equal to, the atomic weight in terms of hydrogen as unity, a conclusion which practically leaves the whole problem of the ultimate constitution of matter where it was, and which is in sharp conflict with the electronic theory of matter, which assumed a number of electrons a thousand times greater. The two other methods of attacking the question depended, the one on the scattering of Röntgen rays by gases, for which the work of Barkla on the ratio of the energy scattered to that in the primary radiation furnished the required data, and the other on the dispersion of light by gases. In the latter method a light wave is considered crossing the atom and subjecting it to the action of the electric field in the wave-front for a period the longer the longer the wave-length of the light. This field affects the displacement of the positively and negatively charged parts of the atom in opposite directions, polarising the atom and increasing the refractive index of the medium. This polarisation and increase of refractive index will in general be the greater the longer the wave-length causing dispersion, and the amount depends upon the relative masses of the positive and negative parts of the atom. For the mathematical development of these three methods the original paper must be consulted. The result that all but about one thousandth of the mass is associated with the positive part of the atom shows that an altogether exaggerated rôle has been attached to the electron in the constitution of matter.

A paper with revolutionary theoretical conclusions, which, however must await further confirmation before being accepted, has been published by H. A. Bumstead² on the heating effects produced by Röntgen rays in different metals. He found that the absorption of equal amounts of Röntgen radiation in lead and in zinc produced approximately double as much heat in the lead as in the zinc. A somewhat complicated method of measurement was employed, depending on a radiometer effect of the heated metal. The hypothesis is suggested

¹ *Phil. Mag.*, 1906, [vi], 11, 769.

² *Ibid.*, 292.

that by means of Röntgen rays the atoms of certain elements may be artificially broken up and the internal energy liberated, causing the excess of the heating effect observed, but such a fundamental conclusion can only be accepted after the most rigorous and exhaustive examination.

γ-Rays.—J. J. Thomson¹ has proved that the effects ascribed by Paschen to the γ -rays carrying negative charges are due to secondary radiation set up by the γ -rays, and that the latter do not carry charges. The same author has shown² that prolonged action of the γ -rays on metals does not cause induced radioactivity, and Bumstead has shown³ that even when arrangements are made to detect an extremely short-lived radioactivity, a negative result is also obtained.

Schmidt found no appreciable γ -radiation accompanying the new β -radiation of radium *B*. Stefan Meyer and von Schweidler⁴ found similarly for radium *E*, the β -ray constituent of radio-lead, that there was no appreciable γ -radiation accompanying the β -rays. If they exist their effect is less than 0.03 per cent. of the β -rays. The same conclusion was indirectly drawn by Eve,⁵ and may be inferred from a paper by Giesel⁶ on " β -Polonium," which, however, there is no doubt owes its β -activity to the presence of radium *E*.

Eve showed that the γ -radiation of uranium and actinium is more readily absorbed than that from radium and thorium, so that by the use of a screen consisting of 1 cm. thickness of lead, the effect of the former may be eliminated, and the rays penetrating such a screen used as a measure of the amount of radium and thorium, for example, in a mineral, without the necessity of powdering it or dissolving it, or even removing it from its containing vessel. On comparing the γ -activity of a kilogram of uraninite from Joachimsthal, which contains all the disintegration products of radium, including radium *E*, in radioactive equilibrium, with that from a known amount of pure radium bromide, which contains no appreciable amount of radium *E*, it was concluded that radium *E* either does not give γ -rays, or more probably that its γ -radiation is, like that of uranium, easily absorbed. However, Meyer and von Schweidler have proved that no γ -rays are emitted. Eve's research had an interesting sequel. Even assuming that the radium *E* give no γ -rays itself, the amount of γ -radiation from the mineral was low, so that the quantity of radium contained in it could only be one half of that to be expected from the work of Rutherford and Boltwood,⁷ who found 0.72 gram radium per ton of uranium. This

¹ *Proc. Camb. Phil. Soc.*, 1905, **13**, 121.

² *Ibid.*, p. 124.

³ *Ibid.*, p. 125.

⁴ *Wien Anzeiger*, 1906, 12; *Sitzung*, April 26th, 1906.

⁵ *Phil. Mag.*, 1906, [vi], **11**, 586; *Amer. J. Sci.*, 1906, **22**, 4.

⁶ *Ber.*, 1906, **39**, 780.

⁷ *Ann. Report*, 1905, 310.

led these investigators to redetermine this constant,¹ with the result that an error was discovered. It was found that about one half of the radium in the standard solution had precipitated on standing without having been noticed. A redetermination gave the value 0.38 gram per ton, a number agreeing with Eve's measurements by means of the γ -radiation, and more nearly what is actually extracted in practice. A later paper by Eve on the relative γ -activity of radium and thorium is considered in the section on radio-thorium (p. 362), and one on the γ -radiation from the earth's surface in the section on radioactive minerals (p. 359).

Action of Ultra-violet Light on Different Metals.—Sir William Ramsay and J. F. Spencer² have investigated the effect of ultra-violet light on a large number of metals and compounds. It is well known that when certain metals, particularly zinc and the alkali metals, are illuminated by ultra-violet light, electrons are expelled from the metal surface, which, if negatively charged, is rapidly discharged by the light. It was found that the order in which the metals arrange themselves in their action under ultra-violet light is the same as in the case of their electro-potentials, exceptions being noticed in the case of those elements, as iron, chromium, nickel, and cobalt, which readily assume the passive form. The compounds examined, sulphides and iodides of the metals, discharged negative electricity like the metals, only more slowly. An examination was also made of the "tiring" of magnesium, zinc, tin, and aluminium exposed to ultra-violet light, the rate of discharge becoming slower with prolonged action. They found on plotting rates of discharge against the times of exposure that the curves showed a number of breaks corresponding with the number of valencies of the metals, except for aluminium, which showed at least five or six breaks. The authors interpret their results on the view that atoms and electrons may be associated in three ways: (1) as in an ion in electrolysis; (2) as in an electrostatically charged object, where the electricity is confined to the surface and may be likened to the wetting of a solid by a liquid; and (3) in a more intimate manner, in such a way that the loss of an electron or electrons is attended by actual transmutation of the original element without the appearance of a positive charge.

The "tiring" of metals under the action of ultra-violet light has also been investigated by H. S. Allen,³ who finds the process can be represented as the sum of two exponentials, as in the case of two successive radioactive changes, and the author suggests that the metal suffers by the process successive transformation into two new modifications, but leaves open for further examination the question of the

¹ *Amer. J. Sci.*, 1906, **22**, 1.

² *Phil. Mag.*, 1906, [vi], **12**, 397.

³ *Proc. Roy. Soc.*, 1907, **78**, A, 483.

nature of the latter and the precise nature of the changes. These results are too recently published for full consideration.

General Properties of Radiations.—Rutherford¹ shows that the distribution of the intensity of radiation in space from a surface coated superficially, as for example in the case of radium C, with a radioactive substance is totally different from what would obtain in the case of a similar surface emitting light or heat. In the latter case the intensity varies with the cosine of the angle between the normal to the surface and the direction of the emitted ray, according to what is known as Lambert's law, and usually explained by supposing that the light comes from a sensible depth below the surface. In the case considered the radiation is strictly superficial, and there is no cosine law. Many beautiful and striking photographs of the effects obtained in consequence are given in the paper. In a paper entitled "Fluorescence and Lambert's Law," R. W. Wood² has imitated Rutherford's effect for radioactive substances with a surface coated with a thin layer of phosphorescent substance, by allowing, for example, a fine dust of Balmain's luminous paint suspended in air to deposit on the surface.

The glow from an uncovered radium preparation in air has been further examined by Sir William and Lady Huggins,³ and by Walter.⁴ The phosphorescent glow extends about 2 cm. in air when examined photographically, and shows the nitrogen bands. The rays from polonium possess the same property, and Walter⁵ has made the interesting observation that the spectrum in the case of radium most resembles the band spectrum of the blue cathode light, whilst that of polonium resembles the red positive glow of a nitrogen vacuum tube. Stark⁶ has shown that the glow in the case of polonium is not affected by an electric field, and argues that the molecules emitting the light are not charged electrically.

A. Miethe⁷ has investigated the action of radium rays, presumably the β - and γ -rays, on a large number of gems, and finds that many show coloration, whereas in the case of those brightly coloured originally the colour is readily changed. A colourless diamond from Brazil showed no coloration after long exposure, but a Borneo stone, originally colourless, turned bright citron-yellow in sixteen days, the colour being only partially discharged on heating to redness.⁸ A bright blue sapphire (corundum) from Ceylon showed a very remarkable series of colour changes under similar treatment, passing through green and bright

¹ *Phil. Mag.*, 1906, [vi], 11, 152.

² *Ibid.*, 783.

³ *Proc. Roy. Soc.*, 1906, 78 A, 212.

⁴ *Ann. Physik.*, 1906, [iv], 19, 1030.

⁵ *Ibid.*, 1906, 20, 327.

⁶ *Phys. Zeit.*, 1906, 7, 892.

⁷ *Ann. Physik.*, 1906, [iv], 19, 633.

⁸ Compare C. W. R., *Nature*, July 19 1906 p. 271.

yellow to a reddish-gold yellow, which was discharged on heating, but returned to some extent when the stone cooled. Ruby, Ceylon chrysoberyl, blue topaz, and Brazilian amethyst showed no change, whilst a colourless quartz rock-crystal turned blue-grey very slowly. Two crystals of Brazilian tourmaline, each colourless at the one end and the other rose-coloured the other bright green at the other end, showed, when the colourless ends were exposed to radium rays, each the same bright coloration as that of the other end of the crystal.

Jorissen and Ringer¹ investigated the action of β -rays of radium on a mixture of hydrogen and chlorine, and found a slow combination, about half a c.c. combining in ninety-six hours. With hydrogen and oxygen there was no combination, and the work of B. Davis and C. W. Edwards,² who found a rapid combination when the radium salt was actually placed in the gas, is probably due to the action of the α -rays in the latter case and may, indeed, be connected with the known large heating effect of the α -rays. Sir W. Ramsay has shown that the β -rays do not decompose liquid water. F. Kohlrausch³ found no sudden change in the conductivity of water when traversed by β -rays of radium, but after prolonged action of the rays the conductivity very slightly increased. Kohlrausch and F. Henning⁴ found that solutions of radium bromide behave as completely normal so far as their conductivity is concerned, and no peculiar behaviour due to the presence of the radium was observed.

General Properties of Radium.—The energy carried away by the penetrating radiations of radium has been the subject of an investigation by Precht,⁵ who finds that the heat evolved, measured in a Bunsen's ice-calorimeter, is increased 10 per cent. when the radium preparation is surrounded by 3 mm. of lead, but is not further increased by increasing the thickness of lead. Obviously some of the β -radiation must be absorbed in the calorimeter itself even with unscreened radium inside, so that the 10 per cent. difference must be for a part only of the energy of the β -rays. The actual heat evolution calculated for 1 gram of the element radium was 122.2 calories per hour unscreened and 134.4 screened. These are considerably higher than the usually accepted values. These experiments recall those of Bumstead with X-rays on metals (p. 351), and may be found to be closely connected with them.

The sample of 25 mg. of anhydrous radium bromide used by Precht in these experiments was sealed in a glass tube 2 mm. in bore and 0.5 mm. wall thickness, and about eleven months after sealing exploded violently.⁶ Precht ascribed the explosion to the generation of suffi-

¹ *Ber.*, 1906, **39**, 2093.

² *Ann. Physik.*, 1906, [iv], **20**, 87.

³ *Ibid.*, 1906, **21**, 595.

⁴ *J. Soc. Chem. Ind.*, 1905, **24**, 266.

⁵ *Ibid.*, p. 96.

⁶ *Phys. Zeit.*, 1906, **7**, 33.

cient gas (helium and emanation) to burst the tube, which, however, would probably require 20 atmospheres pressure. Mercanton¹ found no excess of pressure in a glass tube containing 15 mg. radium bromide after it had been kept sealed for more than three years, and this is to be expected from the common view that the effect is due to electrical strain, as the amount of gas generated from an anhydrous salt is for practical purposes negligible even after long periods. Mercanton also showed that radium emanation does not diffuse at all through glass heated to its softening point. Rutherford has found² that charcoal at the ordinary temperature possesses the property of absorbing the radium emanation completely, so that the escape of the latter from an open vessel containing radium may be entirely prevented if the exit tube is filled with charcoal. Loewenthal³ has investigated the physiological action of the radium emanation dissolved in water and injected into the system. There does not appear to be any injurious effect on healthy subjects, but with patients suffering from chronic rheumatism and similar infirmities there occurs a constant reaction after the treatment, accompanied by inflammation and swelling of the joints, which resembles closely the reaction induced by certain healing springs. The same effect can be produced by inhaling the emanation.

W. A. Douglas Rudge⁴ showed that the action of radium on sterilised gelatin, first noticed by Butler Burke, is exhibited by salts of barium and other metals producing an insoluble sulphate, and is due to the precipitation of the sulphate of the metal by sulphuric acid present in the gelatin. Purification of the gelatin from sulphate stops the action, which can be started again by introducing a soluble sulphate. Radium has no specific action on gelatin apart from the barium present, and other radioactive substances not containing barium are also without effect.

Boltwood⁵ has investigated the escape of the emanation from thin films of radium salts carefully protected from the action of moisture in a desiccator. Mme. Curie has stated that the activity of a radium barium preparation increases to five or six times the initial activity after some months. If first heated to a red heat the maximum ultimately attained is half again as great, while if the preparation is kept fused for two hours the maximum is twice as great. Boltwood evaporated a solution of radium barium chloride to produce thin films, and observed (1) the minimum or initial activity, (2) the equilibrium or maximum activity attained after the films had been kept some weeks in a desiccator, (3) the

¹ *Phys. Zeit.*, 1906, **7**, 372.

² *Nature*, Oct. 25, 1906, p. 635.

³ *Phys. Zeit.*, 1906, **7**, 563.

⁴ *Proc. Camb. Phil. Soc.*, 1906, **13**, 258; *Proc. Roy. Soc.*, 1906, **78**, *A*, 380.

⁵ *Amer. J. Sci.*, 1906, **21**, 409.

amount of emanation actually present in the film under the last conditions, and (4) the total emanation generated in the same time by a similar amount of radium in solution in a closed flask. In this way it was shown that only about 70 per cent. of the total emanation is retained by the dry film and 30 per cent. escapes into the air. The final activity that would be attained if the whole of the emanation were retained is 5.6 times the initial activity. In the case of a film of pure radium bromide, only 45 per cent. of the emanation was retained. Boltwood points out that the ratio 5.6 to 1 is that of the sum of the ranges of the four α -rays to the range of the α -ray from radium itself, but this is probably a mere coincidence.

Radioactivity of Thermal Springs.—A large number of papers, to which only passing reference can be made here, have appeared on the radioactivity of thermal and other springs, and the occurrence of argon and helium in the gases therefrom. H. W. Schmidt and K. Kurz¹ concluded from an examination of the springs of the Grand Duchy of Hesse that nearly all springs contain a radioactive emanation, generally that of radium, but in some few cases also that of thorium. The amount does not depend at all on the depth, temperature, or chemical quality of the spring, but only on the geological relations, springs from igneous rocks being the most active, whilst those from sedimentary rocks, and especially chalk and sand, are least. The most active springs are some well-known healing springs, but by no means all the latter exhibit strong activity. At Kreuznach there is a trace of a radium salt itself dissolved in the water, as Strutt found for the Bath waters. Further reference to this spring is made by Gehlhoff,² and other papers are by Hauser,³ Ewers,⁴ Curie and Laborde,⁵ Dienert and Bouquet,⁶ Mache and S. Meyer,⁷ and Moore and Schlundt.⁸

Radioactive Minerals.—This section usually receives full consideration in the report on Mineralogical Chemistry, and it remains here merely to direct attention to some mineralogical papers by Paul Gaubert on the distribution of uranium at St. Joachimsthal and in Saxony,⁹ and to an especially interesting paper by Marckwald¹⁰ on a new uranium mineral from German East Africa, more radioactive even than the Joachimsthal pitchblende. The mineral occurs disseminated through the mica from the quarries of the Uruguru mountains, and is a black, crystalline pitchblende, more or less weathered into a previously unknown mineral consisting almost entirely of the new compound uranyl carbonate, which is yellow and has never been artificially prepared. Marckwald suggests the name "Rutherfordine" for this

¹ *Phys. Zeit.*, 1906, **7**, 209.

² *Ibid.*, 590.

³ *Ibid.*, 593.

⁴ *Ibid.*, 224.

⁵ *Compt. rend.*, 1906, **142**, 146.

⁶ *Ibid.*, 449.

⁷ *1er Congrès pour l'Étude de la Radiologie, etc.*, Brussels.

⁸ *Amer. Electrochem. Soc.*, Sept. 1905.

⁹ *Le Radium*, 1906, **3**, 1, 132 and 167.

¹⁰ *Centr. Min.*, 1906, **24**, 761.

new mineral, in honour of the distinguished pioneer in the study of radioactivity. The unaltered mineral mainly consists of U_3O_8 (87.7 per cent.), contains 7.5 per cent. of lead, has a sp. gr. 8.84, and is 20 per cent. more active than the pitchblende of Joachimsthal. The weathered mineral contains no less than 96 per cent. of uranyl carbonate and 1 per cent. of lead, with sp. gr. 4.82 and a radioactivity equal to the original pitchblende. It is greatly to be hoped that such a valuable mineral will be found in large quantities.

An analysis of the new mineral thorianite has been published by Büchner,¹ together with the proportion in which the activity is distributed among the constituents. The quantity of helium is given as 8.2 c.c. per gram, and the radioactivity of the sample taken for analysis as 83 per cent. of standard uranium oxide.

Strutt² has found traces of neon, estimated as about 1/300th part, in the helium from two radioactive minerals, zircon and cyrtolite, both containing zirconia, by using Dewar's process of fractionating the gases with charcoal cooled in liquid air. The same investigator has made an exhaustive series of analyses of twenty-eight minerals of the earth's crust for the quantity of radium present.³ He found the igneous rocks contained far more radium than the sedimentary. Granite contains 9.56×10^{-12} gram of radium per gram of mineral, or 25.2×10^{-12} per c.c. of mineral; but these measurements must now all be halved owing to the error previously referred to (p. 353) in the amount of radium in uranium minerals. The amount of radium necessary to maintain the temperature of the earth is calculated by Strutt to be about 1.75×10^{-13} gram per c.c., a quantity which is fifty to sixty times less than the average amount in average igneous rocks, and ten times less than the amount in the poorest samples examined. The conclusion which Strutt draws is that the earth can only consist of a crust of igneous rocks some forty-five miles in depth, the interior being entirely free from radium and composed of a totally different material, which is in agreement with the views of Milne drawn from the study of seismological phenomena. This conclusion has been the source of much discussion, and many other explanations have been advanced. One of these, supported by Lord Kelvin, is that radioactive action ceases at the enormous pressures inside the earth. Soddy⁴ considered that Strutt's results may perhaps be evidence in favour of the view that there is proceeding in nature an as yet undiscovered process, complementary to disintegration, whereby the heavier elements are being slowly built up out of the lighter. Such a process must absorb energy in the same relatively enormous amount in which

¹ *Proc. Roy. Soc.*, 1906, **78**, A, 385.

² *Nature*, Nov. 29, 1906, 102.

³ *Proc. Roy. Soc.*, 1906, **77**, A, 472.

⁴ *B.A. Reports*, York, 1906; *Evolution of the Elements*, footnote.

it is evolved during disintegration. Since the heat that must be evolved in the disintegration of the known amounts of radioactive matter in the earth is far in excess of that required to maintain the loss of heat by radiation and keep the earth temperature constant, and since there is indisputable geological evidence of the constancy of the earth's temperature over a period estimated in hundreds of millions of years, there is at least now no *a priori* objection to the existence of an upbuilding process on the ground that the energy required is not available; but of course the whole subject is only at present in the speculative stage.

Eve,¹ in an examination of the radioactivity of the earth and atmosphere, showed that the ionisation of the latter is caused by the γ -radiation from the earth to the extent of only 1/16th of the total, the remainder being due to the radium emanation present in the atmosphere. He calculates the quantity of radium in the earth's crust necessary to cause the γ -radiation from the surface to be 1.8×10^{-11} gram per c.c., which is of the same order as, but about four times greater than, the average amount found by Strutt in rocks. These two widely different methods of measurement of the radium in the earth's crust are thus as concordant as can be expected considering the nature of the quantity investigated.

Advances in Experimental Methods.—An ingenious device has been suggested by Kurz² for reading the gold leaf of an electroscope. A circular segment is cut out of one side of the leaf near the end to be read, and a quartz fibre is waxed at the two ends and laid across the segment, and attached to the leaf by bringing a heated rod near to the wax. The quartz fibre gives a fine image for reading in the microscope. Bronson³ has worked out a constant deflection method of using the electrometer, in which the ionisation current to be measured is proportional to the deflection of the electrometer needle instead of to the rate of movement, as in the usual arrangement. N. R. Campbell⁴ has devised a null method of working in which the ionisation current to be measured is balanced against the current through a constant volume of gas ionised by a constant quantity of uranium oxide, the pressure of the ionised gas being varied. In this way the measurement is reduced to the adjustment and reading of a gas pressure.

Polonium.—The controversy as to the identity of polonium and radiotellurium, which has long ceased to present more than a nominal interest as to which of the two names should be retained, has now been ended.⁵ Mme. Curie repudiated and gave convincing proof

¹ *Phil. Mag.*, 1906, [vi], 12, 189.

² *Phys. Zeit.*, 1906, 7, 375.

³ *Phil. Mag.*, 1906, [vi], 11, 143.

⁴ *Proc. Camb. Phil. Soc.*, 1906, 3, 132.

⁵ S. Curie, *Phys. Zeit.*, 1906, 7, 146 and 180; Marckwald, *ibid.*, 369; Meyer and von Schweidler, *ibid.*, 257.

against the idea that the polonium as first prepared and named by her gave β -rays or was in a radioactive sense heterogeneous, and protested against the period of decay as published long ago by her being accepted as giving more than the order of the time constant. A new series of exact measurements gives the period one hundred and forty days, which conforms to that of Rutherford for radium *F* and of numerous investigators for "radiotellurium."¹ The greater resemblance of polonium to tellurium than to bismuth chemically is denied, and it is pointed out that in the insolubility of its sulphide in ammonium hydrogen sulphide, and of its oxide in caustic soda, polonium resembles bismuth and differs from tellurium. Mme. Curie considers it self-evident that polonium, the first strongly active substance separated by M. Curie and herself by a method first used by them, must keep the name it received from its discoverers. Marckwald in his communication agrees in future to use the name polonium instead of radiotellurium for his preparations, and it is to be hoped, this being the case, that the name radiotellurium will not be further used. Meyer and von Schweidler² examined polonium from four different sources: (1) the residual induced activity of radium (radium *F*), (2) from radiolead (radium *D*, radium *E*, and radium *F*), (3) "radiotellurium," (4) from radioactive bismuth ("polonium"), and found that all preparations possessed substantially the same rate of decay. The mean of the values for the period was one hundred and thirty-seven days.

Thorium.—A summary of the physical and chemical properties of the disintegration products of thorium is given by von Lerch,³ who himself has been one of the earliest and most fruitful investigators in this field. Our knowledge of the radiothorium, and the position of what has even come to be known as "the thorium question," has been advanced one stage further by the successful partial chemical separation of this constituent from commercial thorium compounds by Elster and Geitel⁴ and G. A. Blanc.⁵ The former separated from the sediment of the hot spring at Baden Baden a preparation with all the characteristics of the thorium radioactivity, but many more times more active, the activity being permanent over short periods. Seventy-five kilograms of these sediments from Bad Nauheim were worked up by Giesel, and gave a gram of a radium-barium preparation of strong activity but practically no thorium activity. Twenty kilograms of the sediments from Bad Kreuznach gave, besides strong radium preparations, small quantities

¹ *Ann. Report*, 1905, 310.

³ *Jahrb. Radioakt. Elek.*, **2**, 463.

⁵ *Ibid.*, 020.

² *Wien. Sitzungsber.*, 1906, **115** II A, 1.

⁴ *Phys. Zeit.* 1906, **7**, 445.

of preparations with thorium activity fifty times that of thorium. With the experience obtained in the working up of these sediments, the separation of radiothorium from commercial thorium salts was attempted. The principle of the method was to precipitate a small quantity of iron with the thorium solution, and to separate the iron from the precipitate with oxalic acid. In this way preparations were obtained decaying rapidly at first (due to the presence of thorium *A* and thorium *B*), but reaching a minimum (radiothorium only), and finally attaining a maximum twice as great (due to the reproduction of thorium *X*, &c.). These preparations consisted of thorium hydroxide with an activity twelve times as great as the original material. The authors point out that radiothorium, like radium, is widely distributed, being found not only in springs and in the earth, but also in some varieties of crude petroleum.

G. A. Blanc¹ first discovered that the deposits from certain hot springs at Echaillon and Salins-Montiers possess thorium activity without any noticeable quantity of thorium being present. Very active preparations could be separated from the deposits possessing the characteristic thorium radioactivity in a very intense degree. He succeeded in separating radiothorium from ordinary thorium preparations² by precipitating barium as sulphate in a solution of thorium nitrate, fusing the precipitate with carbonate of soda, and precipitating the solution of the carbonates in hydrochloric acid with ammonia. A few centigrams of thorium hydroxide with a trace of iron obtained in this way had an initial activity ten times and a final activity thirty times that of ordinary thorium hydroxide. From six kilograms of thorium nitrate was obtained a few milligrams of a preparation initially strongly radioactive but free from emanating power, and ultimately developing emanating power and radioactivity 5000 times that of thorium hydroxide in equilibrium. Thus the separation from ordinary thorium compounds of radiothorium, comparable in radioactivity with the preparations obtained by Hahn from thorianite, has been accomplished; but the complete removal of the active constituent is still very far from being accomplished, and the preparation of "inactive thorium" from active thorium salts has not been effected.

The radioactivity of thorium minerals and salts has formed the subject of investigations by Dadourian³ and Boltwood,⁴ and thorium salts have also been examined from a similar point of view by McCoy and Ross.⁵ The problem was to find the relation between the radioactivity of a thorium mineral or salt (due to radiothorium) and the thorium

¹ *Phil. Mag.*, 1905, [vi], 9, 148.

² *Phys. Zeit.*, 1906, 7, 620.

³ *Ibid.*, 1906, 7, 453; *Amer. J. Sci.*, 1906, 21, 427.

⁴ *Phys. Zeit.*, 1906, 7, 482; *Amer. J. Sci.*, 1906, 21, 415.

⁵ *Ibid.*, 1906, 21, 433.

content, the thorium being in all probability itself without radioactivity. Both Dadourian and Boltwood by different methods found that the radioactivity was proportional to the content of thorium, and therefore that radiothorium must be a true disintegration product of thorium. Dadourian measured the amount of excited activity produced from the solution of a given amount of a thorium mineral, and used this as a measure of the thorium radioactivity. He found this activity, and therefore the amount of radiothorium present, to be proportional to the thorium content of the mineral as determined by analysis. In commercial salts, however, the activity in terms of the thorium content is only about one-half of that in minerals, which points clearly to the separation of a part of the radiothorium during the processes, secret for the most part, by which thorium is commercially extracted from its ores. Boltwood determined the total α -ray activity of several thorium minerals, subtracted the part due to the uranium present as determined by analysis, and found for four minerals the thorium activity per gram of thorium to be a constant. Whereas the specific activity of commercial thorium salts was only one-half of that of minerals, the specific activity of the salts prepared by himself from the minerals was equal to that of the minerals. In view of what has been said (p. 361) on the labour and difficulty in separating radiothorium from thorium, and the fact that in Hahn's work only about 2 per cent. of the radiothorium probably was separated from thorianite, it will be seen that the secret commercial processes are far more effective in removing radiothorium than the known laboratory methods. An investigation of the residues in the manufacture of thorium salts commercially for the radiothorium separated had only negative results. From these researches it is placed beyond doubt that radiothorium is a disintegration product of thorium with a relatively slow period (at least several years), that the change of thorium into radiothorium is probably rayless, and therefore that inactive thorium preparations should be capable of separation. Unless the initial change of thorium were rayless, the close agreement between the results of Dadourian and Boltwood obtained by different methods would not have been shown.

Eve¹ measured the γ -rays given out by known quantities of (1) radium bromide, (2) thorianite, (3) thorium nitrate, the last two containing a known percentage of thorium. He found that the ratio of the γ -activity of the mineral to the salt for quantities containing similar amounts of thorium was 2.5 to 1, again pointing to the poverty of the salt in radiothorium. Hence it is to be expected that the γ -activity of a thorium salt should steadily increase with age as the radiothorium is reproduced, and an earlier suggestion that a kilogram

¹ *Amer. J. Sci.*, 1906, [iv], 22, 477.

of a thorium salt should serve as the standard of γ -radiation is therefore to be abandoned. The γ -activity of pure radium bromide is given as 4.5 million times that of thorium oxide containing the full equilibrium amount of radiothorium.

The diffusion of thorium X in gelatin solutions has been investigated by G. Hoffmann.¹ The diffusion from an under layer to the free surface was followed by measuring the emanation from the free surface, passing a steady air stream over it. He concluded that thorium X diffuses as a single substance, and that radioactive bodies in infinitesimal quantity diffuse according to Fick's law exactly as with substances present in measurable concentration.

Actinium.—There are many problems of interest awaiting solution in connexion with this body, and the almost perfect resemblance from a radioactive point of view between thorium and actinium has been emphasised by several discoveries during the year. Hahn² separated a product he called radioactinium, intermediate between actinium and actinium X , and in every way analogous to radiothorium. If an ignited actinium preparation is dissolved in hydrochloric acid the residue contains relatively a greater proportion of the radioactinium than the solution. A complete separation of the product is obtained when actinium, freed from actinium X by repeated precipitation with ammonia, is treated with sodium thiosulphate in acid solution. Amorphous sulphur is precipitated, and carries down the radioactinium only. Another method is also given depending on the partial precipitation of actinium with ammonia when the active radioactinium is concentrated in the precipitate. The ranges of the various α -rays have already been given (p. 343), and also the conclusion that actinium B is the only β -ray product (p. 340). The period of radioactinium is given as twenty days, and actinium freed from this and the later products possesses no activity, so that the initial change is rayless as in the case of thorium. Godlewski in his separation of actinium X ³ separated unawares some of the radioactinium as well as the actinium X , which accounts for the low activity of the actinium recorded by him. Hahn obtained no evidence of the existence of any residual activity in the case of actinium excited activity pointing to the existence of a possible actinium D , &c., analogous to radium D , radium E , and radium F . On the other hand, Meyer and von Schweidler⁴ detected a small residual activity, $\frac{1}{10000}$ th of the initial, after the ordinary induced activity, produced from the actinium emanation after forty-eight days' working, had been allowed to decay. But instead of being

¹ *Ann. Physik.*, 1906, [iv], 21, 239.

² *Ber.*, 1906, 39, 1605; *Nature*, April 12, 1906, 559; *Phys. Zeit.*, 1906, 7, 855.

³ *Ann. Report*, 1905, 307.

⁴ *Wien Anzeiger*, 1906, 12; *Sitzung.*, April 26.

of a slow period, as in the case of radium, which is to be expected of a product so relatively feeble in activity, it decayed regularly with a period of 11.7 days. The ordinary view leads us to expect that the product of the activity into the period should be approximately the same for all the successive members of a true disintegration series, but the case in question, and also the other new cases of the α -radiation of uranium *X* and thorium *A*, and the β -radiation of radium *B*, constitute exceptions to this rule. We are faced with several examples of ray changes in which the total radiation emitted is very much less than in other cases for changes in the same disintegration series. The most important example of this is probably actinium itself.

Boltwood¹ examined the relative proportion of the α -ray activity of radioactive minerals due to the separate radioactive constituents, and found it could be expressed as the sum of two factors, one depending on the amount of uranium, and the other on the amount of thorium present. McCoy² found that the total radioactivity of five uranium minerals not containing thorium was proportional to the content of uranium being always 4.15 times the activity of the uranium present. This means that actinium must be a product of uranium, and that all the radioactive constituents must be successive members of two series, that of uranium and that of thorium.

The quantity of actinium, determined by separating it from the mineral, is proportional to the uranium. The conclusion was drawn that actinium must be a disintegration product of uranium. But Rutherford and Boltwood, in an examination of the activity of uraninite, found that it was almost accounted for by the radium and uranium present, so that the actinium contributes but a small fraction of the total activity. Yet since actinium gives four α -ray products in its disintegration to five furnished by radium, it is to be expected that the activity contributed by actinium should be comparable to that furnished by radium. In these circumstances Rutherford³ was inclined to view actinium as a simultaneous side-product out of the main line of descent, a suggestion similar to that proposed in the case of radium *A* and radium *B*, and since shown to be unnecessary. Here also the most recent development seems against the view. Boltwood⁴ separated as completely as possible the actinium from a kilogram of carnotite, and measured the amount of radium present in the actinium solution at first, and again 193 days later. In this interval the quantity of radium was found to have increased from 5.7 to 14.2 ($\times 10^{-9}$ gram), and the conclusion was drawn provisionally that actinium is the

¹ *Phys. Review*, 1906, **22**, 320.

² *Phil. Mag.*, 1906, [vi], **11**, 177.

³ *Radioactive Transformations*, p. 177.

⁴ *Nature*, Nov. 15, 1906, p. 54; *Amer. J. Sci.*, 1906, **22**, 537; *Phys. Zeit.*, 1906, **7**, 915.

parent of radium, and that the rate of production is approximately what is to be expected on the view that all the radium in a mineral results from the change of the actinium present. This, if confirmed, shows that actinium is in the main line of descent, and the relations of theory and fact have assumed a kind of stalemate.

Radiolead.—This substance, it is now quite clear, owes its activity to the presence of radium *E* (β -rays) and radium *F* (α -rays) formed from and in radioactive equilibrium with radium *D* (rayless). Although the initial change of radium *D* is slow, the succeeding changes are more rapid, so that the preparation rapidly grows in α - and β -activity, and reaches an equilibrium after a year or two. Meyer and von Schweidler by electrolysing the acetate solution with a current-density of four microamperes per sq. cm. separated polonium (radium *F*). With ten microamperes both polonium and radium *E* are deposited, and with 100 microamperes radium *D* also as well as lead separates. The period of radium *E* is given as 5.02 days. Giesel in his paper on β -polonium gives a somewhat higher period, 6.14 days, whilst Rutherford in his original paper gave 4.5 days.

Elster and Geitel,¹ starting from the observation of N. R. Campbell, that the natural ionisation inside lead vessels is abnormally large, and of A. Wood,² that no emanation is given out by lead solutions, and that the radiations from lead possess a greater penetrating power than the α -rays of radium, made a thorough examination of the activity of ordinary lead. They found that surrounding a zinc vessel with a lead mantle reduced the natural ionisation 11 per cent., showing that the lead gives no appreciable penetrating radiation, but absorbs the penetrating radiation from the earth discovered by Cooke. A kilogram of radiolead obtained from Giesel gave no radium emanation, although the minutest amount could be detected. Using methods which would effect the separation of the radioactive constituents from radiolead, they succeeded in separating from ordinary commercial lead salts preparations with feeble activity. The lead was precipitated successively with hydrochloric acid, sulphuric acid, and hydrogen sulphide, and the last minute precipitate of lead sulphide was feebly active and resembled radiolead. Since radium is very frequently contained in lead ores, it is possible that the radium *D*, which resembles lead chemically, is separated with the lead and is the cause of its feeble activity. This suggests to the authors an elegant piece of work, for old lead—for example, that obtained from the roofs of old buildings—should not be active, as the radium *D* would all disappear in two or three centuries, and unless the lead actually contained radium itself, its activity after this period should have completely decayed.

FREDERICK SODDY.

¹ *Phys. Zeit.*, 1906, 7, 841.

² *Phil. Mag.*, 1905, [vi], 9, 550.

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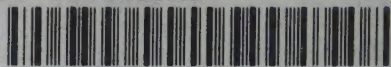
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